SEPARATOR DEVELOPMENT
FOR A HEAT STERILIZABLE BATTERY

Final Summary Progress Report

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ABSTRACT

Two types of ligand-containing polymers were developed that are very promising as separator materials for the sterilizable silver-zinc battery. A film of one, a 0.45:0.55 2-vinylpyridine-methyl methacrylate polymer, had 22 ohm-in. resistivity in 40% KOH and about 1000 psi wet tensile strength after *in situ* saponification during a 120 hr. sterilization in 40% KOH at 135°C. Styrene-maleic anhydride-methyl methacrylate terpolymers also look promising. They require shorter saponification times, have good resistance to zinc dentrites, and give resistivities of about 50 ohm-in.

The program followed to develop these separators included a screening program in which 35 polymers were tested for hydrolytic stability in 40% KOH at 135°C. Three types of polymers, that we found stable, were made into films and comprehensively evaluated: 2-vinylpyridine-methyl methacrylate copolymer; styrene-maleic anhydride copolymers; and polystyrenes with ligand substituents. Film flexibility and durability was improved both by alterations of chemical structure and by improvements in film-forming techniques.

Methods were developed to substitute ligands on polystyrene and styrene-methyl methacrylate backbones.

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I. INTRODUCTION

The primary objective of this program was the development of battery separator materials that will function satisfactorily in a sealed Ag-Zn secondary battery following heat sterilization at 135°C. Several types of ligand-containing vinyl polymers were selected as candidates for this purpose. These polymers have the unique ability to restrict metal ion migration in the cell by chelation of these ions in the form of olated complexes.

Our program was divided into the following four phases:

1.   Preparation of model ligand-containing polymers.

2.   Screening of the model polymers for thermal stability at 135°C and for hydrolytic stability in 40% KOH at 135°C.

3.   Preparation of copolymers and membranes using polymer units that showed high stability in our screening test.

4.   Comprehensive evaluation of our best membranes as battery separators.

In the first part of our program, 35 polymers were screened for thermal stability and for stability in 40% KOH at 135°C. Three general types of polymers that showed high stability in these screening tests were selected for comprehensive evaluation as separator materials. These polymers were:

1.   2-Vinylpyridine-methacrylic (and acrylic) acid copolymers.

2.   Styrene-maleic anhydride copolymers.

3.   Polystyrenes with ligand substituents.

We fabricated membranes and films from polymers of the first two types and evaluated them as separator materials. Several structural modifications of these polymers were made to improve film durability and flexibility while retaining good electrical properties. Our major efforts with the third type of polymer were aimed at the development of synthetic methods for substitution of ligands on polystyrene and/or styrene-methyl methacrylate copolymers.

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II. SUMMARY

Two ligand-containing polymers that were developed as separator materials are highly promising as separators in the silver-zinc sterilizable battery. They are a 2-vinylpyridine-methyl methacrylate copolymer and a styrene-maleic anhydride-methyl methacrylate terpolymer. Dry films of both polymer types are flexible and have approximately 5000 psi tensile strength. Low electrical resistivity of the films is obtained by *in situ* saponification of the methacrylate groups during sterilization in 40% KOH at 135°C. For example, a 0.45:0.55 ratio 2-vinyl pyridine:methyl methacrylate film had 22 ohm-in resistivity in 40 % KOH and about 1000 psi wet tensile strength after sterilization for 120 hrs. Films of the same polymer sterilized in 1M ZnO, 40% KOH had 32 ohm-in resistivity. The terpolymer films saponify within a 60 hr sterilization cycle. These polymers had resistivity of about 50 ohm-in and 800-1000 psi wet strength after 60 hr in 40% KOH at 135°C. Initial tests also indicated that wetted films of the terpolymers resist penetration to zinc dendrites at least as well as Pudo 193.

The above two polymers were developed by first testing candidate polymers for stability in 40% KOH at 135°C to find the most promising types, and then chemically altering the structure of these polymers to give the lowest electrical resistivity compatable with good film durability. In this screening program, 35 polymers were tested as powders. We found that styrene-maleic anhydride, 2-vinylpyridine-methyl methacrylate (-methyl acrylate), 2-vinylpyridine-methacrylic acid and-acrylic acid copolymers, and several polystyrenes with ligand substituents had good stability in 40% KOH. Therefore, we undertook more comprehensive evaluation of these polymers in the form of films and membranes. The stability and durability of these membranes at 135°C in 40% KOH, in 40% KOH saturated with silver oxides, or in 1M ZnO, 40% KOH was determined by measuring the following properties of the membranes before and after exposure.

1. Dimensions

2. Electrolyte absorption

3. Electrical resistance

4. Appearance

5. Tensile strength

In addition, tests to measure pore size and resistance to penetration by zinc dendrites were initiated.

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During development of the 2-vinylpyridine-containing copolymers, several compositions were considered and later excluded for the following reasons:

1) 2-Vinylpyridine-acrylate copolymers, because the methacrylate copolymers gave more durable films.

2) 2-Vinylpyridine-methacrylic and-acrylic acid polymers, since dry films of these crazed excessively and were not usable. Membranes were prepared by depositing these polymers on a polypropylene substrate, but these membranes had large pore sizes and lost some polymer on handling.

3) 2-Vinylpyridine-methyl methacrylate copolymers with methacrylate composition above 65%, because the film durability of the saponified linear copolymers with the high acid content was destroyed in 40% KOH at 135°C, by high solubility.

The styrene-maleic anhydride copolymer is easily hydrolysed at room temperature and has lower electrical resistivity than the 2-vinylpyridine copolymers. However, dry films of the material are extremely brittle. Improvements in flexibility were obtained by plasticization with water and by using styrene-maleic anhydride half-ester or salt copolymers. Durability of the films in 40% KOH at 135°C, however, was marginal and work with the copolymers was suspended in favor of the styrene-maleic anhydride-methyl methacrylate terpolymers.

Polystyrenes with ligand substituents have poor film-forming ability. Several model compounds were prepared and tested in the form of powders for stability in 40% KOH in our screening program. These included poly[vinylbenzyl-X] where X was 1-(2-pyridylmethylamine), catechol, 1-(β-aminoethyl)-2-methyl-2-imidazoline, salicylic acid and 2-(2-pyridylethylamine).

Methods were also developed to prepare polymers with ligand substituents on a styrene-methyl methacrylate backbone. This backbone gives improved film-forming properties to the polymer and also lowers its electrical resistivity after *in situ* saponification of the methacrylate groups.

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III. DISCUSSION OF RESULTS

A. GENERAL

Several candidate polymers were fabricated as membranes and/or films and evaluated comprehensively as separators for the sterilizable silver-zinc battery. Our evaluation of these films and membranes is described in Section III.B. In Section III.C., the screening tests of a wide range of candidate ligand polymers from which we selected these polymers for comprehensive evaluation, are described. The procedures we used to prepare all the polymers are described in Section III.D.

B. COMPREHENSIVE EVALUATION OF LIGAND POLYMERS AS BATTERY SEPARATOR MATERIALS

1. General

Film samples of polymers were tested routinely for stability and durability in 40% KOH at 135°C. Several film samples were also sterilized in 40% KOH saturated with silver oxides or in 1M ZnO, 40% KOH. The following film properties were measured before and after exposure.

1) Dimensions

2) Electrolyte absorption

3) Electrical resistance

4) Appearance

5) Tensile strength

6) Pore size

7) Resistance to penetration by zinc dendrites

These properties were measured following general procedures developed for evaluation of separators for silver-zinc batteries (ref. 1). Details of these tests are described in the Experimental Section. Test results are summarized in Tables 1-4.

Pore size measurements were made principally to determine if the ability of the film or membrane to resist zinc penetration was strongly dependent on small pore size. Our initial tests showed better correlation between the ability to resist zinc penetration and pore size when pore sizes corrected for tortuosity rather than straight through pore sizes were used. Although the correlation

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Table 1

PROPERTIES OF SEPARATORS IN 40% KOH

Ref. No.	Polymer	Dry Thickness (mils)	Original Properties After Soaking Overnight in 40%KOH				Properties After 63 hrs at 135°C in 40% KOH					
			Thickness (mils)	Wt. Gain (%)	Area Retention (%)	ρ ohm-in.	Thickness (mils)	Wt. Gain (%)*	Area Retention (%)*	ρ ohm-in.	Exposure Period (hrs)	Appearance
Pudo 193	Cellophane	0.93	2.8	231	99	4.2	---	---	---	---	---	---
94505	2-VP-methyl methacrylate (0.38:0.62)	1.8	---	---	---	---	7.3	155	85	7.1	134	---
		2.1	---	---	---	---	5.0	87	85	130	63	---
		1.9	---	---	---	---	2.6	45	96	---	39	---
94567	2-VP-methyl methacrylate (0.45:0.55)	1.7	---	---	---	---	3.1	95.5	---	32.3T	113	Smooth & flexible
		1.4	---	---	---	---	2.5	---	86.6	22	113	Smooth & flexible
		1.8	---	---	---	---	4.9	183	72.8	57.1	120	Colorless & smooth
		3.1	---	---	---	---	5.9	69	79.2	1295	120	---
		same film	---	---	---	---	10.2	154		37.4	183	Shrunken
94561	2-VP-methyl methacrylate (0.32:0.68)	1.6	---	---	---	---	---	235	85.8	---	120	Softened & badly deteriorated
89794	2-VP-methacrylic acid (0.54:0.46) on poly-propylene	5.3	6.0	51.6	100	65.4	12.7	159	---	6.3	63	Some mechanical loss of sample
89795	2-VP-methacrylic acid (0.78:0.22) on poly-propylene	9.0	8.9	25.7	100	45.7	16.9	302	---	---	63	Some mechanical loss of sample
100206	2-VP-hydroxyethyl methacrylate	0.9	1.6	37.6	98.4	29,000	1.2	72.9	81.2	249	63	Flexible & smooth; slightly brown colored
							1.0	80.7	78.7	209	79	
Lytron 810	Styrene-maleic anhydride copolymer	3.1	4.9	198	103	---	---	---	---	---	---	---
		5.1	---	---	---	5.7	---	---	---	---	---	---
	with 2% polystyrene on polypropylene substrate	2.8	---	---	---	---	6.7	109	94	22	63	Few holes
		2.9	---	---	---	---	9.3	219	89	10.4	63	No holes
		15.0	14.7	138	103	9.6	12.6	223	96	18.6	63	---
RX347	Styrene-maleic acid half ester copolymer	2.6	---	---	---	---	(225 ohm resistance after 16 hr. soak)	---	---	---		
		---	6.4	---	---	2,730	(159 ohm resistance after 65 hr. soak)	---	---	---		
10024B	Styrene-maleic anhydride-methyl methacrylate terpolymer	1.9	3.2	73.4	101	543	4.7	119	87.3	30.5	63	Flexible & smooth
		1.2TT	---	---	---	---	3.7	122	86.5	37.5	126	Flexible & smooth
		1.3TT	---	---	---	---	2.4	127	99.4	41.4	64	Flexible, few surface bubbles
		1.3	---	---	---	---	1.9	---	---	48	79	---
		1.5	---	---	---	---	2.2	102	94.4	46.7	64	Regular surface
		1.4	---	---	---	---	2.8	117	93.0	42.7	63	Surface irregular
			---	---	---	---	2.7	133	95.7	65.3T	63	Surface irregular
		1.5TT	---	---	---	---	2.7	---	---	69.3T	78	Surface irregular
		1.4TT	---	---	---	---	2.2	160	98.2	94.1T	63	Surface irregular
			---	---	---	---	2.2	138	99.1	101.9T	64	---

* From original dry weight
** Measured in 9 mil area
T Electrolyte contained 1M ZnO
TT Film predried at 0.1mm at 40°C

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Table 1 (Cont.)

PROPERTIES OF SEPARATORS IN 40% KOH

Ref. No.	Polymer	Dry Thickness (mils)	Original Properties after Soaking Overnight in 40%KOH				Properties After 63 hrs at 135°C in 40% KOH					
			Thickness (mils)	Wt. Gain (%)	Area Retention (%)	ohm-in.	Thickness (mils)	Wt. Gain (%)*	Area Retention (%)*	ohm-in.	Exposure Period (hrs)	Appearance
10024A	Styrene-maleic anhydride-methyl methacrylate terpolymer	1.5	2.1	95.3	100	200	2.6	---	100	64.3	62	Flexible & smooth
		1.7	---	---	---	---	3.8	128	93.2	49.3	63	Flexible & smooth
			---	---	---	---	5.0	122	89.9	54	127	Flexible & smooth
		1.7	---	---	---	---	2.8	172	98.3	65.7	63	Flexible & wrinkled
		1.7	---	---	---	---	2.6	144	97	67.0	63	Flexible & wrinkled
		1.5	---	---	---	---	2.9	110	99.3	113T	63	---
		1.5	---	---	---	---	2.9	149	99.3	121T	63	---
10044	Styrene-maleic anhydride-methyl methacrylate terpolymer	1.7TT	2.5	101	104	174	---	---	---	---	---	---
		1.9TT	---	---	---	---	2.7	136	---	62.4	64	Flexible & wrinkled
		1.4TT	---	---	---	---	2.3	146	105	61.2	64	Flexible & wrinkled
		1.5TT	---	---	---	---	2.0	187	105	93.7T	64	Flexible & wrinkled
		1.5TT	---	---	---	---	2.2	179	105	80.6T	64	Flexible & wrinkled
89999	Poly(2-vinyl-4,6-diamino-s-triazine) on poly-propylene	10	8-19	58.2	~90	23.6**	---	---	---	---	---	---
97004	Styrene-4-(methylene-8-hydroxyquinolino)vinyl-benzene copolymer on polypropylene	4.6	4.6	25.4	100	595	---	---	---	---	---	---

* From original dry weight
** Measured in 9 mil area
T Electrolyte contained 1M ZnO
TT Film predried at 0.1mm at 40°C

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Table 2

STABILITY OF SEPARATOR MATERIALS IN 40% KOH SATURATED WITH SILVER OXIDES

Ref. No./ Source	Polymer	Dry Thickness (mils)	Pre-exposure*	Properties After Pre-exposure					Properties after Exposure for 63 hrs. at 135°C to 40% KOH Sat. with Silver Oxides				
				Thickness (mils)	Wt. Gain %	Area Retention %	ρ ohm-in.	Appearance	Thickness (mils)	Wt. Gain% (From Dry)	Area Retention %	ρ ohm-in.	Appearance
94541	2-Vinylpyridine-methyl acrylate (0.75:0.25) copolymer between 4 mil polypropylene		135°-63 hrs / none	12.1	-----	100	822	-----	11.2	------	100	464	-----
89795	2-VP-methacrylic acid (0.78:0.22) copolymer on polypropylene	15.1	r.t.	15.2	34.7	100	46.7	-----	23	82	-----	63	-----
94505	2-VP-methyl methacrylate (0.38:0.62) polymer	1.8 / 2.1 / 1.7	135°-134 hr / 135°-63 hr / none	7.3+1 / 5.0+1	155 / 87	----- / -----	7.1 / 130	----- / ----	6.1+ wrinkled / 5+	156 / 174 / 70.5	100 / ---- / 71	7.7 / ----- / -----	0.057 ohm-in² over 3 ohm-in²
94503	2-Vinylpyridine-methyl methacrylate (0.54:0.46)	2.3	135°-120 hr	11.5	155	99	77.3	-----	7.2	140	99	154	-----
94567	2-VP-methyl methacrylate 0.45:0.55 copolymer	2.5	135°-120 hr	6.2	84	66.6	1092	Colorless;shrunk film, no holes	16.4	150	68.9	10.0	Brown colored, no holes
94567	2-VP-methyl methacrylate 0.45:0.55 copolymer	2.9	135°-120 hr Stretched	6.0	116	83.2	18.8	Colorless with a few holes	9.2	200	73.4	6.1	Brown colored, with many holes
Lytron 810	Styrene-maleic anhydride	3.1	r.t.	4.9	198	103	-----	Flexible	11	160	90	11.2	Brown colored, with holes
Lytron 810	Styrene-maleic anhydride between two 4 mil polypropylene sheets	3.4+ sheets	135°-63hr	16.5	197	100	55	-----	11.5	173	100	89	-----
Lytron 810	Styrene-maleic anhydride in polypropylene wrapper	(19.9)	none	-----	-----	-----	-----	-----	23	180	100	24.9	-----
Lytron 810	Styrene-maleic anhydride on polypropylene substrate	15.0 same sample	r.t. / 135°-63 hr	14.7 / 12.6	138 / 223	103 / 96	9.62 / 18.6	----- / -----	16.0	-----	92.5	7.1	-----
Lytron 810	Styrene-maleic anhydride on 4 mil polypropylene substrate	15	135°-63 hr	12.6(+3)	223	96.3	18.6	Good	16	280	92.5	7.1	Brown colored, slight mechanical loss of polymer
Lytron 810	Styrene-maleic anhydride on 4 mil polypropylene substrate	6.1	none	-----	-----	-----	-----	-----	8.3	154	97.8	28.9	Some mechanical loss of polymer
Permion 2.2XH	Polythylene with acid graft	1.7	r.t.	1.8	78	-----	14.5	-----	2.6	225	89	41.3	Brown-green colored

* r.t. denotes samples that were soaked overnight in 40% KOH at room temperature; 135°C denotes samples that were exposed 40% KOH at 135°C for designated time.

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TABLE 3

TENSILE STRENGTH OF MEMBRANES AT ROOM TEMPERATURE

No.	Polymer	Film State	No. of Specimens	Tensile Strength (psi)
1	2-Vinylpyridine: methyl acrylate copolymer (0.56:0.44)	Dry	4	5800
2	2-Vinylpyridine: methyl methacrylate (0.38:0.62)	Dry	1	5030
3	2:1 Mixture of 2-VP: methylmethacrylate and 2-VP:methacrylic acid copolymers	Dry	3	2140
4	2-Vinylpyridine: Methyl methacrylate (0.45:0.55)	Dry	4	5130
5	2-Vinylpyridine: Methyl methacrylate (0.45:0.55)	Wet with 40% KOH and after exposure at 135°C for 113 hrs in 1M ZnO in 40% KOH	1 1	1080 1420
6	2-Vinylpyridine: Methyl methacrylate (0.45:0.55)	Wet with 40% KOH and after exposure at 135°C for 120 hrs in 40% KOH saturated with silver oxides	1	1250
7	2-Vinylpyridine: Methyl methacrylate (0.45:0.55)	Wet with 40% KOH and after exposure at 135°C in 40% KOH for 120 hrs	1 1 1	1660 828* 620*
8	2-Vinylpyridine: Methyl methacrylate (0.45:0.55)	Wet with 40% KOH and after exposure inside Ag screen in 40% KOH at 135°C for 120 hrs	1 1	195* 300*
9	Polymer in 4 on 4 mil polypropylene substrate	Wet with 40% KOH and after exposure at 135°C in 40% KOH for 120 hrs	1 1	2000 1400

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TABLE 3 (Continued)

TENSILE STRENGTH OF MEMBRANES AT ROOM TEMPERATURE

No.	Polymer	Film State	No. of Specimens	Tensile Strength (psi)
10	2-Vinylpyridine: Methyl methacrylate (0.54:0.46)	Wet with 40% KOH after preexposure at 135°C for 120 hrs to 40% KOH and 63 hrs to 40% KOH saturated with silver oxides	1 1	1000 388**
11	Styrene-maleic anhydride copolymer (1:1)	Dry	4	1760
12	Styrene-maleic anhydride copolymer (1:1)	Wet with water	1	940
13	Styrene-maleic anhydride copolymer (1:1)	Wet with 40% KOH	8	220***
14	Styrene-maleic anhydride (Lytron® 810)	Wet with 40% KOH and after exposure in 40% KOH for 63 hrs at 135°C	1	273*
15	Styrene-maleic anhydride (Lytron® 810) on 4 mil polypropylene substrate	Wet with 40% KOH and after exposure in 40% KOH for 63 hrs at 135°C	1 1	1670 1000
16	Styrene-maleic anhydride in 4 mil polypropylene wrapper	Wet with 40% KOH after exposure at 135°C for 120 hrs to 40% KOH and 63 hrs to 40% KOH saturated with silver oxides	2	1370
17	Styrene-maleic anhydride methyl methacrylate terpolymer No. 10024A	Dry	2 2	5330 3070
18	Styrene-maleic anhydride methyl methacrylate terpolymer No. 10024A	Wet with 40% KOH and after exposure in 40% KOH for 63 hrs at 135°C	2 2	820 1000

TABLE 3 (Continued)

TENSILE STRENGTH OF MEMBRANES AT ROOM TEMPERATURE

No.	Polymer	Film State	No. of Specimens	Tensile Strength (psi)
19	Styrene-maleic anhydride-methyl methacrylate terpolymer No. 10024A	Wet with 40% KOH and after exposure in 40% KOH for 79 hrs at 135°C.	2	763
20	Styrene-maleic anhydride methyl methacrylate terpolymer No. 10024A	Wet with 40% KOH and after exposure in 1M ZnO in 40% KOH for 63 hrs at 135°C	3	1075
21	Styrene-maleic anhydride methyl methacrylate terpolymer No. 10024B	Dry	2	4850
22	Styrene-maleic anhydride methyl methacrylate terpolymer No. 10024B	Wet with 40% KOH and after exposure in 40% KOH for 63 hrs at 135°C	2	760
23	Styrene-maleic anhydride methyl methacrylate terpolymer No. 10024B	Wet with 40% KOH and after exposure in 40% KOH with 1M ZnO for 63 hrs at 135°C	2	820
24	Styrene-maleic anhydride methyl methacrylate No. 10044	Dry	2	5935
25	Styrene-maleic anhydride methyl methacrylate No. 10044	Wet with 40% KOH and after exposure in 1M ZnO in 40% KOH for 63 hrs at 135°C	4	300
26	Pudo 193	Dry	1	25,000

* Film specimens contained wrinkles.
** Visible nicks in sample.
*** Crosshead speed 5 in/min; elongation at break to 115%.

Table 4

ELECTRICAL RESISTIVITY, PORE SIZE AND RESISTANCE TO ZINC PENETRATION OF SEPARATOR MATERIALS

Sample No.	Polymer	History of Sample	Dry Thickness (mils)	Ratio Change Thickness to Wet Thickness	Specific Resistance (ohm-in)	Porosity from Electrolyte Absorption (1)	Effective Porosity from Conductivity (2)	Straight-Through Pore Size, μ	Tortuosity Factor (3)	Corrected Pore Size, μ (4)	Zinc Penetration Factor (5)
Chemstrand	Acrilan®, 3 oz/yd	Soaked overnight in test solution	7.3	0	3.1	0.302	0.283	1.0	1.03	1.03	~12
Lytron® 810	Styrene-maleic anhydride	"	6.4	0.33	10.1	0.513	0.0872	0.012	2.43	0.029	33,44(5)[6]
89795	2-Vinylpyridine-methacrylic acid on poly-propylene (0.78:0.22)	"	6.8	0	113	0.083	0.00778	0.93	1.03	0.96	10 (2)[6]
94567	2-Vinylpyridine-methyl methacrylate (0.45:0.55) on polypropylene	Heated at 135°C for 120 hr. in 40% KOH	5.8	0.23	12.7	0.485	0.0692	1.89	2.64	5.0	14 (2)[6]
94503	2-Vinylpyridine-methyl methacrylate (0.54:0.46)	Heated at 135°C for 120 hr. in 40% KOH and 63 hr. in 40% KOH sat. with silver oxides	2.3	0.68	153	0.325	0.0057	0.045	7.5	0.34	17 (1)[6]
94505	2-Vinylpyridine-methyl methacrylate (0.38:0.62)	Heated at 135°C for 134 hr. in 40% KOH and for 63 hr. in 40% KOH saturated with silver oxides	1.8	0.71	7.7	0.402	0.114	0.21	1.87	0.39	~12
Pudo 193	Cellophane	Soaked overnight in test solution	1.0	0.67	4.2	-----	-----	---	---	<0.03	368 (5)
10024A	Styrene-maleic anhydride-methyl methacrylate terpolymer	Soaked overnight in test solution	2.5 wet / 2.5 wet	---- / ----	200 / ---	----- / -----	----- / -----	---	---	<0.03 / <0.03	440 (3) / 157 (3)
10024A	Styrene-maleic anhydride-methyl methacrylate terpolymer	Sterilized 60 hrs	2.8 wet	----	65	-----	-----	---	---	<0.03	110 (1)
10024B	Styrene-maleic anhydride-methyl methacrylate terpolymer	Sterilized 60 hrs	2.0 wet	----	540	-----	-----	---	---	<0.03	506 (4)

Footnotes:

1) Pore volume from electrolyte absorption ÷ Wet volume of Separator

2) Resistivity of 40% KOH (ohm-in) ÷ Resistivity of Separator in 40% KOH = $0.879 \div \rho$ separator in ohm-in

3) $\sqrt{\dfrac{\rho_{membrane} \text{ (Effective Porosity)}}{\rho_{KOH}}}$

4) Tortuosity factor x straight-through pore radius

5) Ave. Time To Traversal (min) ÷ sample wet thickness (mils)

6) No. of samples tested for zinc penetration

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is not conclusive, the results indicate that pore sizes under 0.02 μ are probably needed for these type membranes to have good resistance to zinc penetration.

2. 2-Vinylpyridine-methacrylic and acrylic acid copolymers

Two forms of membranes made with the above copolymer systems were tested. One type of membrane was prepared by casting 2-vinylpyridine(2VP)-methacrylic acid copolymers into a porous polypropylene substrate. It was necessary to use a supported membrane with these polymers because they form extremely brittle films. Membranes with acceptably low resistance that survived sterilization in 40% KOH or 40% KOH saturated with silver oxides were prepared by this technique (89794 and 89795 in Tables 1, 2 and 4). In fact, the sterilization treatment caused the membranes to swell and gain considerably more weight above what they had gained on soaking at room temperature. However, these membranes characteristically had certain disadvantages: (1) some mechanical loss of polymer during handling and sterilization; (2) membrane thickness greater than unsupported films; (3) problem in obtaining homogeneous surfaces; and (4) relatively large pore sizes (Table 4).

The second type of membrane was prepared by *in situ* saponification during sterilization of 2-VP-methyl acrylate or 2-VP-methyl methacrylate films. Both ester copolymers form excellent films. However, films made from the methacrylate copolymers retained shape and strength after saponification and sterilization much better than those made from acrylate esters.

Several saponification conditions were tried with these polymers to determine the best way of preparing the free acid groups while retaining film integrity. The methacrylate polymers are more resistant to saponification and required longer reaction times under all conditions. The best medium found was 40% KOH at 135°C. Other hydrolysis media that were tried, but found either ineffective within reasonable reaction times and/or dissolved the resultant polymer are listed below:

1) 1N HCl saturated with NaCl

2) 1N NaOH

3) 1N alcoholic NaOH saturated with NaCl

We also found it necessary to support these films during hydrolysis in order to maintain reasonable film shape. The following methods of supporting these films were tried: (1) holding the films between two pieces of silver screen, (2) clamping the film in a Teflon frame, (3) fastening the film on a Teflon cylinder with silver wire, and (4) casting film on polypropylene substrate and saponifying the resulting membrane without

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additional support.

Small samples were successfully saponified to films with acceptably low electrical resistance by all the above methods, but the use of the cylinder support and use of polypropylene substrate gave films with fewer mechanical irregularities.

A series of 2-VP-methyl methacrylate copolymers with varying ester contents were tested to find the best ratio for both good film durability and low electrical resistance. The optimum ester (acid) concentration in the linear polymer was found to be 55 to 65%. Membranes with acid contents under 50% had higher initial electrical resistances and larger increases in resistance after exposure to 40% KOH saturated with silver oxides. We found that linear copolymers with acid contents over 70% were not usable because of their high solubility in 40% KOH at 135°C.

The film durability during sterilization was dependent on film quality, as well as acid content of polymer and the method used to support the film. The most durable films were prepared by casting a 14% polymer solution in methanol onto a polypropylene slab at room temperature. A Gardner Blade was used as leveler. Several films of the 0.45:0.55 2-VP-methyl methacrylate copolymer with dry thickness 1.5 to 2.5 mils that were made by this method retained film durability after saponification and sterilization for 120 hrs. in 40% KOH at 135°C. Tensile strengths of exposed films are shown in Table 3 and electrical properties in Table 1. Films with strengths under 1000 psi contained wrinkles due to insufficient support during saponification. These films tolerate the presence of either zincate or silver ion species during sterilization very well. For example, samples that were sterilized in 1M ZnO in 40% KOH had tensile strengths of 1080 and 1420 psi and electrical resistance of 32 ohm-in in 40% KOH.

3. Styrene-maleic anhydride polymers

a. Styrene-maleic anhydride copolymer

Styrene-maleic anhydride membranes have the advantage of very low electrical resistance in 40% KOH. This copolymer, however, gives rather hard films. Therefore, both supported membranes and films were tested. The supported membranes were prepared by casting the copolymer into a polypropylene substrate. This type membrane has electrical resistance under 20 ohm-in and survives sterilization satisfactorily, but the membranes are relatively bulky (Table 1).

The durability of unsupported films was extremely dependent on the quality of the film. Samples containing crevices from uneven or rapid evaporation of solvent did not survive

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sterilization. We found that samples prepared by casting a 20% solution of Lytron® 810 polymer, in methyl ethyl ketone were free of surface irregularities and survived sterilization.

The flexibility of dry films made with Lytron® 810 polymer, can be improved by plasticization. Films containing 2% polystyrene, 2% stearic acid, 15% tricresyl phosphate or water were prepared. Water proved to be the most effective plasticizer. For example, we found that films stored in 100% humidity could be bent and handled easily without prewetting in 40% KOH. In contrast, films stored in 80% humidity were still fragile, while films stored in water were flexible, but developed holes when sterilized. The water-stored film was probably weakened by slight solution of polymer on addition of 40% KOH, since the polymer is soluble in dilute caustic. A film that was pre-exposed to 100% humidity survived sterilization without developing holes. Its wet tensile strength was 273 psi.

b. Salts of styrene-maleic acid

Films having somewhat greater flexibility at moderate humidities can be obtained with the salt copolymers than with the corresponding anhydride polymer. Reported (ref. 2) characteristics of films cast from water made from this type of copolymer are shown in Table 5. These films become very brittle in dry atmospheres.

Salt copolymers that are soluble in organic solvents can also be made by partial neutralization. Films that have moderate flexibility at 80% humidity were prepared by 25% neutralization of Lytron 810 polymer with lithium hydroxide.

c. Styrene-maleic anhydride half-ester copolymers

Increased flexibility of the styrene-maleic anhydride type polymer can also be obtained by using half-ester polymers. Samples of a styrene-maleic acid half ester, RX-347, that has good film flexibility when dry were sterilized for 60 hrs. However, the exposed films were very soft and broke up on handling. The poor durability was probably the result of its low molecular weight (about 20,000) since chemical composition after hydrolysis during saponification is almost the same as for the copolymer, Lytron®810. Therefore, a sample of a n-octyl half ester copolymer was prepared from Lytron 810 polymer (molecular weight about 50,000). The quality of films prepared from this polymer were not very much improved, however. Test results with this type of polymer indicated that polymers with much higher molecular weight are needed to improve the strength of films derived from both the anhydride and half-ester copolymers. However, work with the half-ester and salt copolymers was abandoned in favor of the terpolymers described below because these terpolymers gave superior films.

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Table 5

PROPERTIES OF FILMS OF LYTRON 810 SALTS (REF. 2)

Salt	Tensile Strength (psi)	% Elongation	% Relative Humidity
Li	3800	5	50
K	2500	10	50
Li	2400	20	75
K	900	57	75

d.   Styrene-maleic anhydride-methyl methacrylate terpolymers

These type polymers give very flexible, strong films
that can be handled easily at low humidities. A comparison of
the electrical properties (Table 1) and tensile strength (Table 3)
was made on 1.2 to 1.9 mil thick films of these polymers before
and after sterilization in 40% KOH and in 1M ZnO, 40% KOH. Data
from these tests show that their separator properties are very
similar to the 2-vinylpyridine-methyl methacrylate copolymers.
However, the terpolymer films have some advantages. First, the
films of the terpolymers show very little tendency to shrink
during sterilization. Secondly, the films appear to resist zinc
penetration better(Table 4). Pore size measurements by the
electrolyte permeability method showed that the pore size of
both fresh and sterilized films was very small. Thirdly, the
terpolymer films swell and have some conductivity in 40% KOH at
room temperature due to their maleic anhydride content. The
vinylpyridine copolymers are hydrophobic before saponification.

The tensile strengths of dry films of these terpolymers
were all approximately 5000 psi. Sterilized films showed wet
tensile strength of 800-1000 psi (Table 3).

The resistivity of these films decreased after steriliza-
tion (e.g. 64.3 ohm-in, after, compared to 200 ohm-in, before,
for 10024A). Resistivity of the three terpolymers tested was
greater in 40% KOH, 1M ZnO than in 40% KOH. The same difference
was noted with samples sterilized in 1M ZnO, 40% KOH directly as
in samples sterilized in 40% KOH and then immersed in 1M ZnO,
40% KOH at sterilization temperature for 16 hrs. Only films of
terpolymer 10024B had near acceptable resistivity (under 60 ohm-
in) in the zincate electrolyte (65, 69 ohm-in). The results
indicate that a terpolymer with higher maleic anhydride content is
needed to meet all separator specifications.

4.   Polystyrenes with Ligand Substituents

A membrane of the 4-(5-methylene-8-hydroxyquinolino)vinyl-
benzene-styrene 0.27:0.73 copolymer was prepared by casting a
20% solution of polymer in benzene onto a 3-mil polypropylene
substrate. This membrane had high electrical resistance (2.75
ohm-in^2). Our test results indicate that a higher degree of
substitution of ligand in this type of polymer is needed to
lower resistance to a usable range for this program.

5.   Poly(2-vinyl-4,6-diamino-s-triazine)

Usable membranes of this polymer were prepared by casting
a solution containing 20 weight-% polymer in 10% aqueous HCl on
porous 3-mil polypropylene substrate. A sample of this film
gained 58% in weight after soaking overnight in 40% KOH and had
a resistance of 24 ohm-in. This indicates that amino substituents

may be as effective as carboxylic acid and hydroxyl groups in lowering resistivity of organic polymers. However, this particular polymer is not stable in 40% KOH at 135°C. A sample of the polymer in powder form hydrolyzed and evolved ammonia during the 60-hour screening test.

C. SCREENING TESTS FOR POLYMER STABILITY

1. Thermal Stability at 135°C

The thermal stability of our candidate polymers was determined by isothermal gravimetric analysis. Samples were heated at 135°C in a nitrogen atmosphere for 60 hours. The test procedure is described in the Experimental section. The extent of degradation was determined by measuring weight loss and by comparing the infrared spectra of the polymers before and after exposure.

Table 6 lists data from these tests. It appears that the initial weight losses are due to adsorbed volatiles, principally water, in the samples.

Several polymers with carboxylic acid substituents dehydrated partially to anhydrides under the test conditions. The infrared spectra of these exposed samples slowed increases in absorption at 5.55 to 5.60μ, characteristic of the anhydride group. The extent of dehydration varied from slight for the 2-vinylpyridine-methacrylic acid copolymers to almost quantitative dehydration of the ethylene-maleic acid copolymer.

No other definite changes in polymer structure were detected from the infrared spectra of the other samples. With the exception of poly(styrene azosalicylic acid) and poly(styrene azo-8-hydroxyquinoline), that contain nitro impurities, all polymers can be considered stable.

2. Stability in 40% KOH at 135°C

a. Test Procedure

The following procedure was used to test the stability of our ligand-containing polymers in strong caustic.

  (1) Powdered samples of each polymer were immersed in 40% KOH contained in a Teflon lined stainless steel bomb.

  (2) The bombs were heated in an oven controlled at 135±1.5°C for at least 60 hours.

  (3) The polymer was recovered and examined.

Table 6

THERMAL STABILITY OF MODEL POLYMERS AT 135°C IN NITROGEN ATMOSPHERE

Source/Ref.	Polymer	Wt. Loss (%) After x Hrs. 24 hours	After x ( ) hours	Change in IR Spectra After Exposure	Change in Appearance After Exposure
Gelvatol® 1-90	Poly(vinyl alcohol)	1.7	1.7(48)	- - -	none
Formvar® 95-15S	Poly(vinyl formal)	0.63	0.54(69)	Dec. 8-10μ	- - -
Butvar® -76	Poly(vinylbutyral)	5.63	6.44(95)	Sl. Dec. 12.4μ	Yellowed and fused
89782	Poly(p-aminostyrene)	3.4	3.7(71)	broadened	none
89772	Poly(aminonitrostyrene)	3.2	4.3(95)	none	none
	Poly(styrene azo-salicylic acid)	7.3	8.7(72)	general broadening	- - -
	Poly(styrene azo-8-hydroxyquinoline)	6.9	7.4(95)	general broadening	- - -
89932	Polyvinylbenzyl-catechol	0	0(68)	Sl. Inc. 6.0-6.2μ	Darkened
89775	Poly(vinylbenzyl-salicylic acid)	4.7	5.2(93)	general broadening	none
89789	Poly[N-(2-pyrimidyl)aminostyrene]	7.9	7.9(65)	none	none

Table 6 (Cont.)

THERMAL STABILITY OF MODEL POLYMERS AT 135°C IN NITROGEN ATMOSPHERE

Source/Ref.	Polymer	Wt. Loss (%) After x Hrs. 24 hours	After x ( ) hours	Change in IR Spectra After Exposure	Change in Appearance After Exposure
89784	Poly[vinylbenzyl-1-(β-aminoethyl)-2-methyl-2-imidazoline]	0	0(71)	none	none
89754	Polyvinylbenzyl-2-(2-pyridylethyl)amine	2.8	4.3(83)	Sl. Inc. 5.8-6.14μ	Darkened
Monsanto CD-600	Styrene-acrylonitrile-butadiene polymer	0.8	(+0.4)(95)	general broadening	fused, slight yellowing
Lytron®100	Styrene-methyl-acrylate copolymer	1.4	1.7(71)	---	none
Lytron®810	Styrene-maleic anhydride	4.7	4.7(116)	none	---
Monsanto EMA-22	Ethylene-maleic acid copolymer	13.8	13.8(70)	inc. 5.4-5.8, 6.95,7.5μ dec.5.92,7.15μ	none
Monsanto EMA-54	Ethylene-sodium maleate copolymer	4.5	5.1(95)	dec. 5.9μ	none
Gantrez®AN-169	Methylvinylether-maleic anhydride copolymer	5.5	5.5(89)	none	none
Monomer-Polymer Laboratories	Poly-N-vinyl-carbazole	0.33	0.47(72)	---	---

Table 6 (Cont.)

THERMAL STABILITY OF MODEL POLYMERS AT 135°C IN NITROGEN ATMOSPHERE

Source/Ref.	Polymer	Wt. Loss (%) After x Hrs. 24 hours () hours	Change in IR Spectra After Exposure	Change in Appearance After Exposure
PVP-NP-K30 (General Aniline and Film Corp.)	Poly-N-vinyl-pyrrolidone	6.4 6.6(114)	general broadening	- - -
B.A.S.F.	Poly(N-vinylimidazole)	5.7 5.7(63)	none	slight yellowing
89929	Polyethyleneimine-N-(5-methylene-8-hydroxyquinoline)	5.5 6.2	Broadened, inc. 6.1-6.2µ	Darkened
89768	2-Vinylpyridine-methacrylic acid copolymer	5.3 5.7(70)	5.6µ appears	- - -
89771	2-Vinylpyridine-methyl acrylate polymer	5.2 3.8(68)	Unchanged	Fused

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Table 6 (Cont.)

THERMAL STABILITY OF MODEL POLYMERS AT 135°C IN NITROGEN ATMOSPHERE

Ref/Source	Polymer	Weight Loss, %		Change in IR Spectrum After Exposure	Change in Appearance After Exposure
		24 hr.	(X) hr.		
94503	2-Vinylpyridine-methyl methacrylate copolymer	8.5	8.5(70)	none	v. slight yellowing
94509	2-Vinylpyridine-meth- acrylic acid-butylvinyl ether terpolymer	15.5	17.3(71)	5.55, 5.70μ new; 9.55, 11.0μ dec.	none
94507	2-Vinylpyridine-meth- acrylic acid-butylvinyl ether terpolymer	9.0	ca.25*(71)	5.55, 5.70μ new; 5.75, 11.0, 12.0μ dec.	fused, porous from gas evolution
94528	2-Vinylpyridine-diethyl fumarate copolymer	5.8	5.1(48)	general broadening 5.80μ decrease	fused and black
94533	Poly(2-vinyl-4, 6-diamino- triazine)	1.4	0.5(65)	none	none
CN 54	Styrene-acrylonitrile copolymer	0.53	0.76(66)	none	none
97004	Poly[4-5(methylene-8- hydroxyquinolino) vinylbenzene]-styrene	0	1.4(66)	3.0, 6.5μ decrease	sintered
94554	Polyvinylbenzylchloride- methyl methacrylate	0.3	2.0(120)	5.65μ new; general broadening	
	Poly[N-(ar-vinylbenzyl) iminodiacetic acid]	2.5	5.6(60)		

*mechanical loss of sample by overflow from sample crucible during gas evolution.

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In this test, all material that dissolved in the 40% KOH test solution, both stable but soluble fractions of polymer and soluble degradation products, was considered as weight lost.

The procedure for recovery of the polymers necessarily varied because of the different solubility characteristics of the polymers. The following tabulation illustrates the general procedure used to remove KOH residues from the recovered samples:

Polymer Type	KOH Removal Method
A. Water – insoluble	Multiple washing with water
B. Water-soluble	
1. Alcohol-insoluble	Multiple washing with alcohol
2. Alcohol-soluble	Extract with organic solvent and recover by evaporation of solvent
C. Salt-forming	Neutralize and wash free of salts as for A or B above

The recovered products were checked for possible degradation by comparing weight, appearance, infrared spectra, softening points, solubility characteristics, and viscosity before and after exposure. These data are summarized in Table 7.

b. **Analysis of Polymers Exposed to 40% KOH at 135°C**

   1) **2-Vinylpyridine-(meth)acrylic Acid and Ester Copolymers**

Ligand-polymers of this type that we evaluated were highly resistant to 40% KOH. Weight losses were low and properties of recovered polymers were essentially unchanged. For example, a 0.57:0.43 copolymer of 2-vinylpyridine-methacrylic acid suffered only 3.2% weight loss and had identical viscosity in 0.45% dimethylformamide solutions before and after exposure.

A copolymer of ethyl-2-vinylpyridine-methacrylic acid in ratio 0.58:0.42 showed much higher weight loss (16.5%) than other polymers of this type. This weight loss may be due to loss of low molecular weight soluble portions rather than degradation resulting from the presence of the ethyl group. Properties of recovered polymer were essentially unchanged.

The 2-vinylpyridine-methyl acrylate copolymer was also recovered essentially unchanged after exposure except for complete saponification of its ester group. The physical properties of the exposed sample were compared to those of a sample of this copolymer that was saponified in 1N NaOH.

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Table 7

STABILITY OF MODEL POLYMERS IN 40% KOH AT 135°C

Source/Ref.	Polymer	Wt. Loss (%) After 63 Hours	Change in Appearance	Change in IR Spectra	Viscosity Comparison [n]Before	[n]After	Solvent	Softening Point, °C Before	After
89768	2-Vinylpyridine-methacrylic acid	3.2	sl. yellow		1.08*	1.08*	Dimethyl-formamide	215-220	177-185
89771	2-Vinylpyridine-methyl acrylate copolymer	(+4)	-	14.3 appears	0.38	0.41	Dimethyl-formamide	135-247	140-240
89787A	Ethylvinylpyridine-methacrylic acid copolymer	16.5, 13.1	darkened	Dec.6.15μ	1.08*	1.10*	Dimethyl-formamide	195-210	205-220
94503	2-Vinylpyridine-methyl methacrylate (0.54:0.46)	10.0	light brown	none(E) none(A)	1.56(E) 1.39(A)	1.53*(E)	Dimethyl-formamide	125-230(E) 220-265(A)	
94505	2-Vinylpyridine-methyl methacrylate (0.38:0.62)	8.7	light brown	none(E)	1.67(E)	1.72*(E)	Dimethyl-formamide	115-240(E)	
94507	2-Vinylpyridine-methacrylic acid-butylvinyl ether terpolymer	25.1	darkened	Dec.9.8, 11.0μ	1.08	1.13*	Dimethyl-formamide	95-150	
94509	2-Vinylpyridine-methacrylic acid-butylvinyl ether terpolymer	11.1	black	sl.dec. 11.0μ	1.08	1.08*	Dimethyl-formamide	190-240	
94562	2-Vinylpyridine-methyl methacrylate (0.23:0.77)	Sample dissolved in 120 hr. test							
Monomer-Polymer Laboratories	Poly-N-vinyl-carbazole	2.1	None	Dec.3.48 and 10.4μ	0.61	0.63	Dimethyl-formamide	224-265	223-280
Lustrex®	Polystyrene	1.0	fused	--	0.52	0.57	Benzene	125-135	109-125
Amberlite® 120HCP	Sulfonated polystyrene	(+1.9)	None					over 300	over 300
89782	Poly(p-amino-styrene)	2.8	None	None				230 to over 300	230 to over 300
89752	Polyvinylbenzyl-chloride	0.6	-	None	insoluble after test			245-	245-
89777	Poly[vinylbenzyl-1-1-(2-pyridylmethylamine)]	3.6	None	None				over 300	over 300

Table 7

STABILITY OF MODEL POLYMERS IN 40% KOH AT 135°C

(Continued)

Source/Ref.	Polymer	Wt. Loss (%) After 63 Hours	Change in Appearance	Change in IR Spectra	Viscosity Comparison			Softening Point, °C	
					$[\eta]$ Before	$[\eta]$ After	Solvent	Before	After
89784	Poly[vinylbenzyl-1-1-(β-aminoethyl)-2-methyl-2-imidazoline]	4.1	None	None	–	–	–	over 300	over 300
89932	Polyvinylbenzyl-catechol	10.0	Darkened	inc.6.0-6.2µ	–	–	–	over 300	over 300
89754	Polyvinylbenzyl-2-(2-pyridylethyl)amine	9.7	Darkened	5.9-6.1 inc.	–	–	–	over 300	over 300
89775	Poly(vinylbenzyl-salicylic acid)	16.2	None	Inc. 6.68 Dec. 6.0,8.95, 11.45				over 300	over 300
89929W	Polyethyleneimine-N-(5-methylene-8-hydroxyquinoline)	3.3	None	Inc. 6.1,7.15µ broadening				140-	160-240
CN-54 Monsanto	Styrene-acrylonitrile copolymer	9.4	fused	inc. 6.1-6.2µ	1.49*	1.48*	Dimethyl formamide	120-220	125-205
CD-600 Monsanto	Stryene-acrylonitrile-butadiene polymer	25.5	darkened and fused (NH₃ odor in KOH)	very minor	1.30*	1.28*	Dimethyl formamide	120-220	117-205
Lytron® 810	Styrene-maleic anhydride copolymer	up to 21	darkened	None	1.83**	1.56**	Dimethyl formamide	235-288	230-285
PVP NK-30	Poly-N-vinyl-pyrrolidone	16.0	darkened & hardened	general broadening	insoluble after test			180-210	208-275
FORMVAR® 95-15S	Poly(vinylformal)	20.8	darkened & hardened	5.8 gone; 8.1 dec.; 6.2 - 6.5µ inc.	insoluble after test			145-210	over 300
Butvar® 76	Poly(vinylbutyral)	19.5	hardened	broadened	insoluble after test			80-200	95-185
Butvar® 72 A	Poly(vinylbutyral)	22.3	hardened	Hydroxyl, 7.0, 7.5, 8.1 dec; 6.45µ appears	insoluble after test			95-215	175-over 300
Gelvatol® 1-90	Poly(vinyl alcohol)	47.3	colored black	6.5, 7.3µ appears	1.09	only 12% of recovered solid was soluble	H₂O	225-230	over 300

Table 7

STABILITY OF MODEL POLYMERS IN 40% KOH AT 135°C

(Continued)

Source/Ref.	Polymer	Wt. Loss (%) After 63 Hours	Change in Appearance	Change in IR Spectra	Viscosity Comparison [η]Before [η]After Solvent			Softening Point,°C Before After	
89772	Poly(aminonitro-styrene)	28.3	darkened	broadened; 7.5μ dec.	--		--	--	--
	Poly(styrene-azo-salicylic acid)	23.9^{ττ}		broadened	insoluble polymer			over 300	--
	Poly(styrene-azo-8-hydroxyquinoline)	25.3^{τττ}		inc. 6.2, 7.5μ dec. 6.7, 7.3, and 8.2μ	insoluble polymer			over 300	--
BASF	Poly(vinylimidazole)	39.7, 40.3	became black	none	insoluble after exposure			210-300	over 300
EMA® 22	Ethylene-maleic acid copolymer		soluble in 40% KOH						
Gantrez® AN-169	Methylvinylether-maleic anhydride copolymer	(100)	soluble in 40% KOH	--	--		--	--	
Acrilan®	Polyacrylonitrile	Sample dissolved							
94533	Poly(2-vinyl-4,6-diamino-s-triazine)	Sample dissolved							

τ   Comparisons made with acid form of hydrolyzed polymers
*   Relative viscosity at 0.5% concentration. All viscosities were measured at 30°C
** Relative viscosity of acid form at 0.15%.
ττ Loss after exposure for 63 hours longer was 20.2%
τττ Loss after exposure for 63 hours longer was 18.9%

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Total recovery of 2-vinylpyridine-methyl methacrylate polymers was over 90% with the exception of the polymer with high acid content (77%) that dissolved on hydrolysis (120-hr exposure). These polymers are only partially saponified during the 60 hr exposure period in contrast to the more easily saponified acrylate esters that saponify completely. The recovered polymers were isolated in two fractions. The saponified fraction was soluble in dilute caustic. Its spectrum in the acid form was identical to that of a sample of polymer saponified in alcoholic 1N NaOH. The spectrum of the potassium salt of this fraction showed no residual ester funtionality. The spectrum of the water-insoluble fraction was identical to that of the original ester form of polymer. The percentage recovered in the ester form was 72% for the 0.54:0.46 polymer (94503) and 51% for the 0.38:0.62 polymer (94505).

Weight losses of the 2-vinylpyridine-methacrylic acid-butylvinyl ether terpolymers were higher than would be expected. No changes in chemical structure of recovered polymers were detected and it appears that this weight loss is due to solubility of low molecular weight fractions in 40% KOH.

2) Candidate Polymer Backbones

Polystyrene and poly-N-vinylcarbazole were recovered essentially unchanged after exposure.

3) Polystyrenes with Ligands on Methylene Linkage

The methylene linkage on polystyrene was found to be stable under test conditions. Therefore, screening tests of polystyrenes containing ligand substituents on a methylene linkage appear to measure the stability of the ligand substituent itself. The stability of the methylene linkage was confirmed by almost quantitative recovery of polyvinylbenzylchloride after exposure. This polymer crosslinked slightly during exposure since the exposed sample was insoluble in dioxane and other solvents for the linear polymer. However, the infrared spectrum of the exposed sample showed that the major part of the chloromethyl groups was still present (7.96 μ).

The fact that this chloromethyl group was not hydrolyzed under test conditions is surprising. However, analysis of degradation products of polymers tested point up the fact that 40% KOH acts principally as a dehydration agent. Only very reactive groups such as esters and anhydrides hydrolyze in 40% KOH under the test conditions.

Several polymers that have methylene linkages between the ligand groups and the polymer backbone were tested. Two of these, poly[vinylbenzyl-1-(2-pyridylmethylamine)] and poly[vinylbenzyl-1-(ß-aminoethyl)-2-methyl-2 imidazoline], were recovered

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essentially unchanged after the test.

Two other polyvinylbenzyl polymers tested had slightly higher weight losses. These polymers had catechol and 2-(pyridylethyl) amine as ligand substituents and lost about 10% weight on exposure. Changes in structure of recovered polymers detected in the infrared spectra were minor. Both polymers showed increase in absorption at $6 \pm 0.2\mu$, some of which may be caused by differing amounts of adsorbed water on these hydroscopic polymers. Quinone formation from air oxidation is a possible source of these absorptions in the catechol polymer.

Another polymer of this type, poly(vinylbenzylsalicylic acid), had a weight loss of 16%. Changes detected in its infrared spectra indicate this weight loss may be due to decarboxylation.

4) Other Substituents on Polystyrene Backbone

Poly(aminostyrene) and poly(aminonitrostyrene) were tested since unreacted amino and nitro groups are present in some polymers derived from poly(aminostyrene). Poly(aminostyrene) was stable and was recovered unchanged. The poly(aminonitrostyrene) sample, however, was degraded extensively. This sample showed no absorption in the infrared at 7.5μ characteristic of the nitro group after exposure. The weight lost (28%) by the sample is equivalent ot loss of the nitro substituent from the polymer, but degradation was probably a complicated process involving partial reduction of the nitro group and oxidation of the polymer. The dark red coloration of the KOH solution, visible after the test, indicates the probable presence of partially reduced ionized nitrogen species (ref. 3). These results indicate that it is necessary to use poly(aminostyrene) free of all nitro groups in polymer preparations to insure stability, but unreacted amino groups can be tolerated.

Two polymers with the azo linkage on polystyrene backbones were tested: polystyrene-azo-8-hydroxyquinoline and polystyrene-azosalicylic acid. Both polymers lost approximately 25% of their weight during 63 hours' exposure. The same samples when exposed to a second 63 hour cycle continued to lose weight at approximately the same rate. The low stability of these polymers may be caused, in part, by the presence of nitro substituent impurities.

The sulfonic group on the polystyrene backbone appears to have good stability in 40% KOH. A sample of Amberlite 120 HCP was recovered without loss of weight.

5) Polymers Containing Acrylonitrile

Acrylonitrile was potentially a useful monomer for this
program because of its ability to copolymerize with some monomer-
ligands that do not homopolymerize. Two polymers containing
acrylonitrile, a styrene-acrylonitrile copolymer (Monsanto CN-54)
and a styrene-acrylonitrile-butadiene terpolymer (Monsanto CD-600),
were tested. Comparison of the infrared spectra of exposed and
fresh samples indicated that most of the nitrile substituent
survived unchanged. Comparison of viscosity of polymer solutions
and softening points of these polymers before and after also
indicated little attack by KOH. Slight hydrolysis of the ter-
polymer did occur; the odor of ammonia was evident in the sample
after exposure. However, the extent of hydrolysis of both these
samples was very minor compared to that of the homopolymer, poly-
acrylonitrile which dissolved completely under the test conditions.
The lower stability of the homopolymer may be the result of the
greater solubility of its hydrolysis product, poly(sodium acryl-
ate), in 40% caustic.

In conclusion, these test results indicated that physical
properties of copolymers containing acrylonitrile probably would
not be effected adversely by the sterilization cycle. However,
these materials probably could not be used as separator materials
because of detrimental effect of even small amounts of ammonia
on the silver oxide electrode.

6) Maleic Anhydride Copolymers

The recovered, exposed samples of a styrene-maleic anhyd-
ride copolymer had almost identical properties to a sample hydro-
lyzed in 1N NaOH except viscosity was slightly lower. The dif-
ficulty in recovering these water-soluble polymers limited
accuracy in measuring weight loss. Weight loss of an exposed
sample recovered by acidification and washing with dilute HCl was
21.5% compared to 23% for a control sample hydrolyzed in 1N NaOH
and recovered in the same way.

Samples of ethylene-maleic acid copolymer (EMA-22) and
methylvinyl ether-maleic anhydride copolymer (Gantrez AN-169)
were found to be soluble in 40% KOH.

7) Poly(Vinylacetals) Derived from Poly(vinyl alcohol)

The acetal group itself,
$$\left[\begin{array}{c} -CH-CH_2-CH-CH_2- \\ OO \\ CH \\ | \\ R \end{array} \right]_n$$

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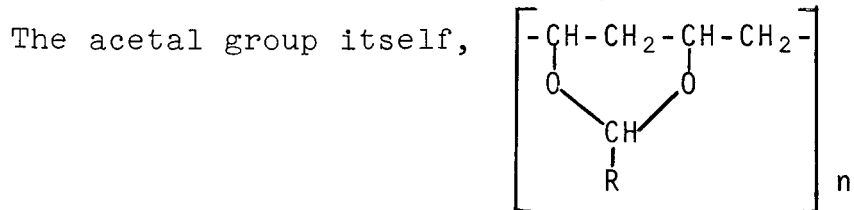
appears stable under the test conditions. However, stability of the acetal polymer appears to be limited by degradation of unreacted hydroxyl groups on these polymers. These conclusions are based on the following evidence:

1. The magnitude of absorptions in the infrared, attributed to formal and acetal functions (ref. 4), are approximately the same in the samples before and after the exposure period, although exposed samples show general broadening in these regions. (Disappearance of acetate function is detected in these spectra).

2. Weight loss of all acetal polymers was appreciably less than weight loss by poly(vinyl alcohol). Degradation of poly(vinyl alcohol) was extensive as shown by a weight loss of 47% and the fact that the recovered product was largely insoluble in water indicating extensive crosslinking.

3. Weight loss by acetals with different substituents but identical acetal functionality were about the same.

In conventional methods of preparing acetal polymers the highest acetal functionality obtained is 80-88%. Therefore, this class of compounds was dropped from consideration.

8) Poly-N-Vinylpyrrolidone

In the test in 40% KOH this polymer degraded to an insoluble, presumably crosslinked product with 16% loss of weight. Its spectra in the infrared was unchanged after exposure except for a general broadening. In 1N NaOH the pyrrolidone ring is reported to open to form an amino acid and the polymer remains soluble (ref. 5).

9) Poly(N-Vinylimidazole)

A sample of this polymer, supplied by Badische Anilin and Soda-Fabrik AG, lost 39% of its weight during exposure in 40% KOH at 135°C. The recovered fraction apparently was highly crosslinked since its softening point was higher than the fresh sample, and it was no longer soluble in water. Its spectrum in the infrared was unchanged, however.

D. SYNTHESIS OF LIGAND-CONTAINING POLYMERS

1. General

Two general methods were used to prepare the ligand-polymers. One method involved substitution of ligands on a

polymer backbone by a coupling reaction. This method was used to substitute ligands on polystyrene via methylene, azo, or amino linkages. Polymers prepared by this method are described in Section III.D.3 of this report.

A limited amount of work was also done using this method to substitute ligands on poly(vinyl alcohol) by reaction with ligands containing aldehyde substituents to form an acetal polymer. This work was terminated when the results of our stability tests of these acetal polymers in 40% KOH showed that they did not have the required stability for this application.

The second method used to prepare ligand-polymers was by the copolymerization of two ligand monomers to form a chelate group directly in the 1:1 copolymer. Polymers that were prepared by this method are described in Section III.D.2.

The ligand groups incorporated into these polymers are given in Table 8. These particular chelating groups were chosen for the following two reasons. First, they form stable chelates in basic media. Second, they should have goood stability in strong caustic at 135°C.
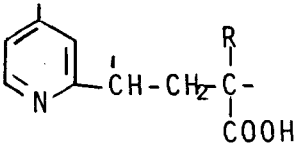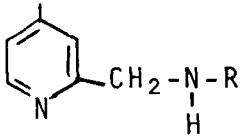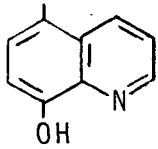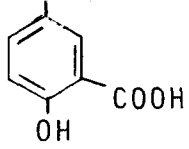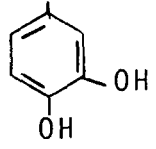
2. Vinylpyridine Copolymers

Chelation sites were introduced directly into a polymer by copolymerization of two ligand monomers that form a chelating site in each 1:1 copolymer unit. For example, copolymerization of 2-vinylpyridine and methacrylic acid yields a polymer with this ligand grouping:

$$\left[\underset{N}{\bigcirc} -CH-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{COOH}{|}}{C}}-CH_2 \right]_n$$
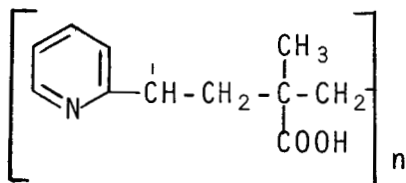
Copolymers with different monomer ratios were prepared by bulk polymerization of the above reactants with azo-bis isobutyronitrile catalyst following a procedure described by Alfrey and Morawetz (refs. 6,7). Our screening tests showed these polymers to be exceptionally stable in 40% KOH. However, they gave brittle films. Therefore, several types of 2-vinylpyridine copolymers, discussed below, were prepared to find polymer configurations with the optimum combination of film-forming ability and low electrical resistance. Data describing these polymers are in Table 9. They were prepared by bulk polymerization in a nitrogen atmosphere. Details of their preparation are described in the Experimental Section.

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Table 8

LIGAND GROUPS FOR INCORPORATION INTO VINYL POLYMERS

Name	Structure	Donor Groups	
1. Pyridine-acids		N	O
2. Aminopyridines		N	N
3. 8-Hydroxyquinolines		N	O
4. Salicylic Acid		O	O
5. Catechol		O	O

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a. 2-Vinylpyridine-Methyl Methacrylate and Acrylate Copolymers

Copolymers of this type give the corresponding acid copolymers by *in situ* saponification in base during sterilization. All the ester polymers yielded flexible films. Acid copolymers derived from the methacrylate ester copolymers retained shape and strength better than those derived from acrylate ester. Therefore, several copolymers with a range of ester contents from 46% to 77% were prepared to find the best ratio for both good film durability and low electrical resistance.

b. 2-Vinylpyridine-Diethyl Fumarate Copolymer

The polymer prepared by copolymerization of a 1:1 charge of monomers had a 0.66:0.34 monomer composition. Its molecular weight, based on viscosity, was very low and the polymer gave very brittle films.

c. 2-Vinylpyridine-Methacrylic Acid-Butylvinyl Ether Terpolymers

A technique for improving the film-forming characteristic of methacrylic acid copolymers directly is to incorporate butylvinyl ether units into the polymer chain. Two terpolymers of 2-vinylpyridine, methacrylic acid and butylvinyl ether were prepared. A polymer having approximately equal mole ratios of the three monomers had improved film-forming characteristics but had a high electrical resistance (31 ohms-in^2). A terpolymer with lower butylvinyl ether content (0.35:0.55:0.10) did not give a usable film. Viscosity measurements of both these polymers indicate that their molecular weights are low.

d. 2-Vinylpyridine-Maleic Anhydride Polymers

This type was chosen both because of its easy conversion to the free acid form and because it does not give any volatile products on hydrolysis. Several attempts were made to prepare 2-vinylpyridine-maleic anhydride-butylvinyl ether terpolymers and 2-vinylpyridine-maleic anhydride copolymers with both free radical catalysts and zinc chloride catalysts. All polymers were brown powders, and measurements of viscosity of solutions of two of the polymers indicated that they have low molecular weights. The maleic anhydride content of these polymers, especially the copolymer, are very high. These properties suggest that the products are low molecular weight complexes.

e. 2-Vinylpyridine-Hydroxyethyl Methacrylate Copolymer

A sample of this copolymer was prepared by bulk polymerization of equal mole quantities of the monomers with azo-bis-isobutyronitrile catalyst. We expected that the hydroxyl substituent

Table 9

COMPOSITION OF LIGAND COPOLYMERS AND TERPOLYMERS

Ref.	Monomers[a]	Mole Ratio Monomers	Reaction Time(hr)[b] at 60°C	Conver-sion wt-%	Solvent non-solvent Used for Purification	Mole Ratio Monomers in Polymer[c]
89765	2-VP: Methyl acrylate	0.33:0.67	4-1/3		benzene/hexane	0.56:0.44
94540	2-VP: Methyl acrylate	0.33:0.67	3-1/2	32.5	benzene/hexane	0.56:0.44
94541	2-VP: Methyl acrylate	0.60:0.40	3	35	benzene/hexane; acetone/hexane	0.75:0.25
89728	2-VP: Metha-crylic acid	0.50:0.50	6(70°C)	13	methanol-benzene/ acetone	0.58:0.42
89794	2-VP: Metha-crylic acid	0.60:0.40	4(70°C)	34	-/acetone	0.57:0.43
89795	2-VP: Metha-crylic acid	0.67:0.33	4(70°C)	43	-/acetone	0.78/0.22
89787A	Ethyl-2-VP: Methacrylic acid	0.50:0.50	6(70°C)	8	-/acetone	0.58:0.42
94514	2-VP: Maleic anhydride:Butyl-vinyl ether	0.33:0.33: 0.33	4	--	acetone/hexane	0.25:0.64: 0.11
94525-1	2-VP: Maleic anhydride:Butyl-vinyl ether	0.40:0.20: 0.40	18	10	acetone/hexane	0.32:0.59: 0.09
94548	2-VP: Maleic anhydride	0.67:0.33	4	6.7	-----/methanol; -----/hot benzene	0.16:0.84
94528	2-VP: Diethyl fumurate	0.50:0.50	18	14	benzene/hexane	0.66:0.34
94509	2-VP: Metha-crylic acid: Butylvinyl ether	0.25:0.50: 0.25	21[d]	20	Benzene-methanol/ hexane and acetone/ hexane	0.35:0.55: 0.10
94507	2-VP: Metha-cryclic acid: Butylvinyl ether	0.15:0.30: 0.55	51	8	benzene-methanol/ hexane	0.33:0.34: 0.33
94524	2-VP: Metha-crylic acid: Butylvinyl ether	0.33:0.33: 0.33	70	2.5	acetone/hexane	0.55:0.34: 0.11
94503	2-VP: Methyl methacrylate	0.50:0.50	7	16	benzene/hexane	0.54:0.46
94505	2-VP: Methyl methacrylate	0.30:0.70	7	20	benzene/hexane	0.38:0.62
94567	2-VP: methyl methacrylate	0.30:0.70	7	22	benzene/hexane	0.45:0.55
94561	2-VP: Methyl methacrylate	0.20:0.80	5	13	benzene/hexane	0.32:0.68
94562	2-VP: Methyl methacrylate	0.10:0.90	4	12	benzene/hexane	0.23:0.77

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10024A	Styrene:Maleic anhydride:Methyl methacrylate	0.50:0.25: 0.25	1	30	acetone/hexane	(0.51:0.34: 0.15)[f]
10024B	Styrene:Maleic anhydride:Methyl methacrylate	0.40:0.20: 0.40	6	30	acetone/hexane	(0.51:0.30: 0.19)[f]
10044	Styrene:Maleic anhydride:Methyl methacrylate	0.40:0.40: 0.20	1	47	acetone/hexane	(0.51:0.38: 0.11)[f]
94551	Vinylbenzylchloride: Methyl methacrylate	0.50:0.50	33[e]	33	benzene/hexane	0.56:0.44
94577	Vinylbenzylchloride: Methyl methacrylate	0.50:0.50	43[e]	43	benzene/hexane	0.53:0.47

---

a   2-VP is 2-vinylpyridine
b   0.02 weight % azo-bis-isobutyronitrile catalyst
c   Based on elemental analysis
d   Temperature reached 132°C for about 15 min. last hour
e   0.2% azo-bis-isobutyronitrile
f   Based on neutralization equivalents and elemental analyses

would make the copolymer more hydrophilic than the corresponding
methyl ester copolymers and facilitate saponification in 40%
KOH. A film made from the copolymer wetted readily with water,
but the saponification rate of the ester groups in 40% KOH was
only slightly accelerated.

3. Styrene-Maleic Anhydride-Methyl Methacrylate Terpolymers

This type of terpolymer was prepared to obtain films
containing the maleic anhydride group that have greater flexi-
bility when dry than films of styrene-maleic anhydride copolymers.
Three terpolymers were prepared by bulk polymerization of the
monomers with 0.02% azo-bis-isobutyronitrile catalyst at 60°C.
Flexibility of films prepared from the three polymers was excel-
lent.

Viscosity measurements indicate that molecular weights of
these polymers are higher than commercial styrene-maleic anhydride
(e.g. Lytron® 810 is 50,000). Intrinsic viscosity in methyl
ethyl ketone of polymers 10024A, 10024B and 10044 was respectively,
0.92, 1.78 and 1.13. An estimate of the molecular weight of
10024B using known constants for styrene-methyl methacrylate
copolymers (ref. 8), as follows,

$$[n] = kM_n^a = 1.54 \cdot 10^{-4} M_n^{0.68}$$
$$\text{gives } \bar{M}_n = 93,000.$$

Composition of the products was calculated from neutraliz-
ation equivalents together with elemental analysis. Reproducible
neutralization equivalents were obtained by analysis of acetone
solutions of the polymer. Details of this analysis are in the
Experimental section.

4. Substitution of Ligands on Polystyrene

### a. Through a Methylene Linkage

Ligands were substituted on polystyrene through the
methylene group by reactions of these ligands with chloromethylated
linear polystyrene. This intermediate was prepared by chloro-
methylation of polystyrene in dichloroethane with chloromethyl-
methylether and a stannic chloride catalyst using the procedure
described by Gregor and coworkers (ref. 9). Samples of poly-
styrene with molecular weight ca·20,000 and ca·100,000 were
chloromethylated. We found it necessary to use high dilution
for reactions involving a high molecular weight polystyrene
(ca·100,000) in order to maintain sufficient solubility of the
product and to prevent by-product crosslinking. Polymers pre-
pared by this method had approximately 40% chloromethyl sub-
stitution.

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Two reaction sequences with polyvinylbenzylchloride were used for substitution of the ligands. The first method involved the reaction of the polymer with reactive amino-substituted ligands. This route is illustrated in the preparation of poly-vinylbenzyl-2-(2-pyridylethyl)amine.
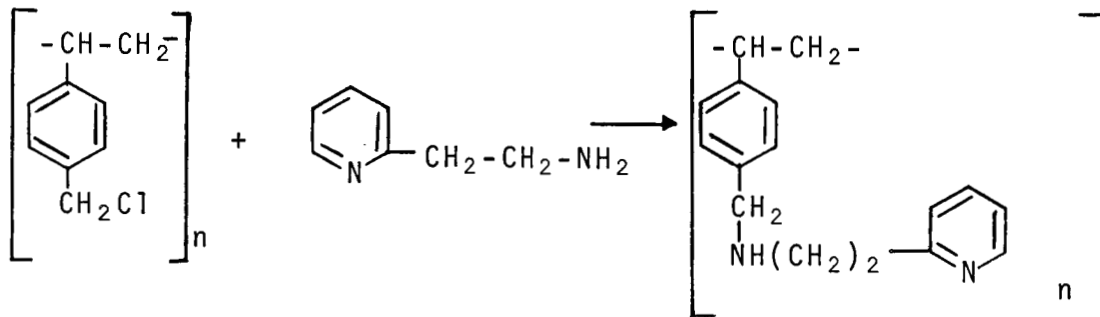

Other ligand-containing polymers prepared by this route were polyvinylbenzyl-2-pyridylmethylamine and polyvinylbenzyl-1-(β-aminoethyl-2-methyl-2-imidazoline. The amino group on 5-aminosalicylic acid and the alkyl hydroxyl group on 5-(4-hydroxy-butoxymethyl)-8-hydroxyquinoline did not react.

The Friedel-Crafts reaction was the second method used for reaction of ligands with polyvinylbenzylchloride. Poly-vinylbenzylcatechol and polyvinylbenzylsalicylic acid were prepared by this route using reaction conditions developed by Kun (ref. 10) for substitution of hydroquinone on polystyrene.
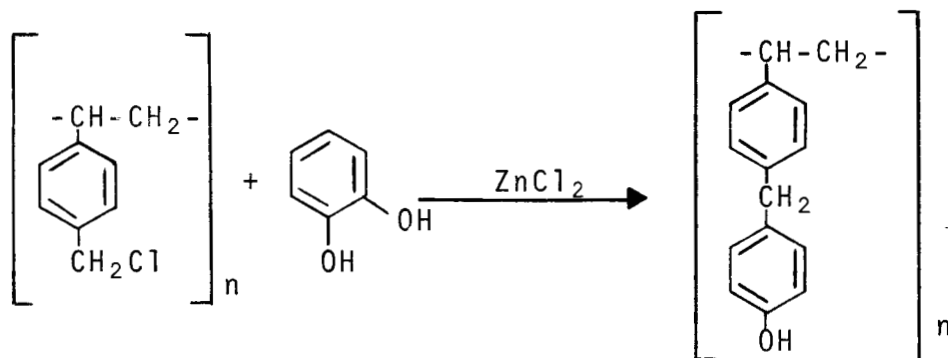
Polyvinylbenzylcatechol

We also found that 8-hydroxyquinoline could be substituted on polystyrene by a Friedel-Crafts reaction using a chloromethyl group on the ligand, 5-chloromethyl-8-hydroxyquinoline hydrochloride. In this preparation polystyrene with molecular weight 20,000 was used.

OH N·HCl CH₂Cl + [CH-CH₂] → AlCl₃ → [CH-CH₂]ₘ [CH-CH₂]ₙ CH₂ N OH
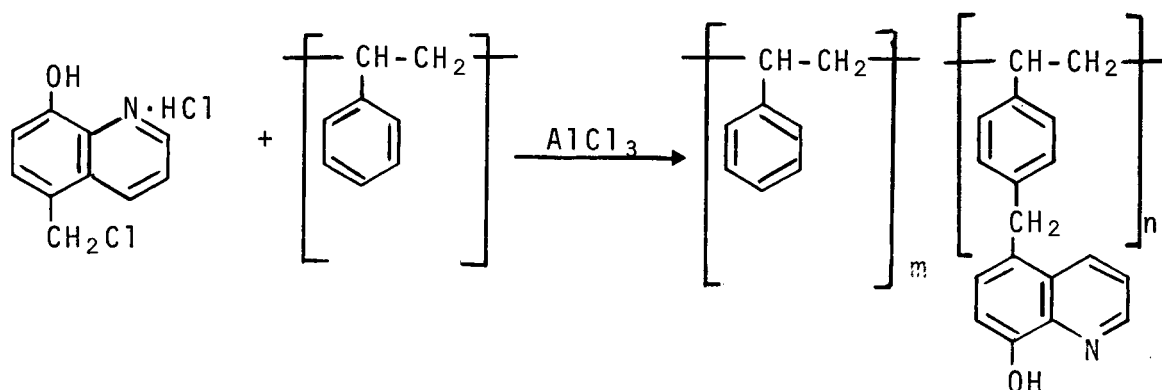
The product obtained using 0.5 mole of chloromethyl compound per styrene unit contained about 27% substitution and had a softening range of 123-145°C.

The products of substitution of high molecular weight polystyrene characteristically had poor film-forming properties. The products had low solubility in common organic solvents, and in some cases, appeared to be partially crosslinked. We concluded that to insure good film properties in the product polymer, the substitution reaction should be carried out on a flexible backbone polymer, such as styrene-methyl methacrylate. The reaction sequence with amines is most suitable with the copolymer. Reactions with a copolymer backbone are described in Section 5.

b. Through an Azo Linkage

The ligands, 8-hydroxyquinoline and salicylic acid, were substituted on the polystyrene backbone through an azo linkage using a reaction sequence developed by Davies and co-workers (ref. 11). This reaction sequence involves the following four steps:

(1) Nitration of polystyrene to form poly (p-nitrostyrene).

(2) Reduction of the nitro groups with stannous chloride in HCl to give poly (p-aminostyrene).

(3) Diazotization of the amino groups, and

(4) Reaction of the diazonium compound with the ligand hydroxyl groups.

Substitution of the ligand at the azo linkage occurs *para* to the ligand hydroxyl groups.

The products prepared by this sequence from linear, high molecular weight polystyrene were not pure azo-substituted linear polymers but contained free nitro functions. These polymers were infusible at 300°C and practically insoluble in all organic solvents. It is possible to eliminate the nitro group impurities present by using a modified reaction sequence employing the method of Zenftman (ref.12) for nitration of polystyrene. However, because of the poor mechanical properties of these polymers, this was not done.

c. Through an Amino Linkage

Pyrimidine was substituted on polystyrene (through an amino group) by reaction of 2-chloropyrimidine with poly(aminostyrene) in pyridine to give a ligand substituent with NH and N donor groups.

$$\left[\text{CH-CH}_2\right]_n\text{-NH}_2 \;+\; \text{(pyrimidine)Cl} \;\longrightarrow\; \left[\text{CH-CH}_2\right]_n\text{-NH-(pyrimidine)}$$
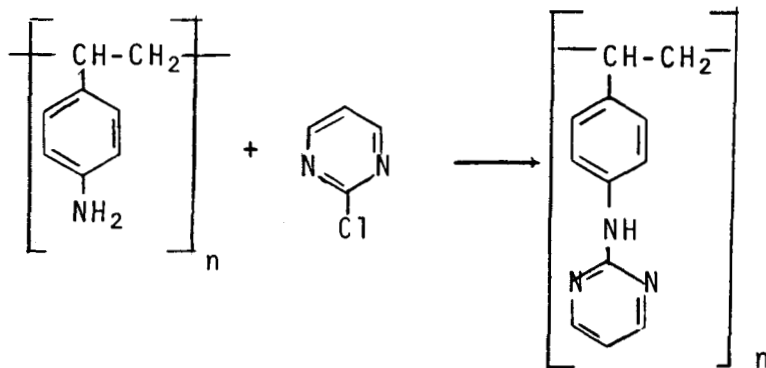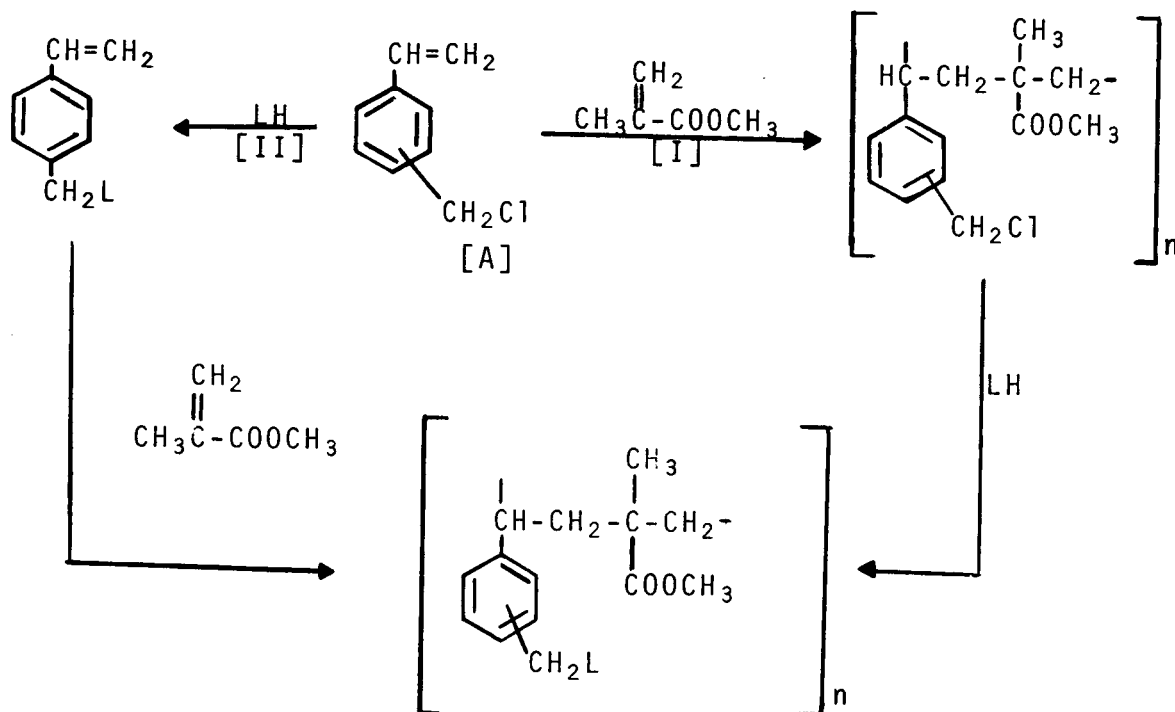
The poly(aminostyrene) used in this preparation was prepared by the modified reaction sequence described above and was free of nitro groups.

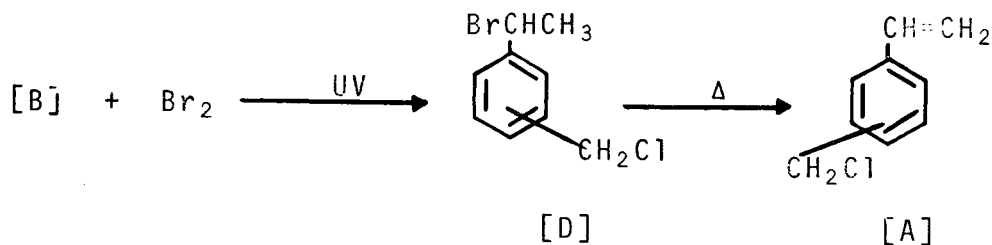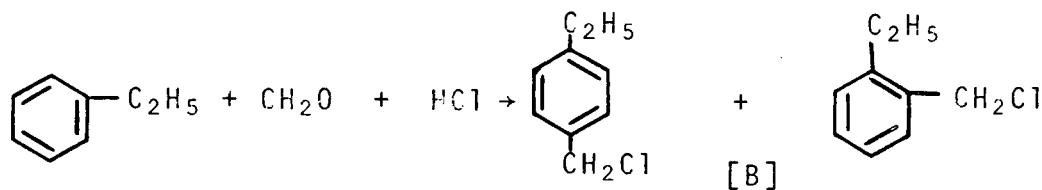### 5. Substitution of 8-Hydroxyquinoline on Styrene-Methyl Methacrylate Copolymer

The ligand 8-hydroxyquinoline is especially useful as a substituent because it forms strong chelates and because it has high thermal and hydrolytic stability. To obtain a usable separator membrane with this ligand, it is necessary to substitute it on a backbone that is both flexible and has low electrical resistance. The relatively low contribution 8-hydroxyquinoline substituents make to lower electrical resistance of polystyrene was illustrated in the model polymer described in Section III.B.4. Methyl methacrylate was chosen as the comonomer with styrene for three reasons. First, it copolymerizes well with styrene monomer; second, it increases the flexibility of the polymer; and third,

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it lowers the resistivity of the polymer after saponification.

Two routes, illustrated below, for preparation of these polymers were tried. In this scheme LH represents the ligand.

$$
\text{[A]} \xrightarrow[\text{[II]}]{\text{LH}} \quad , \quad \text{[A]} \xrightarrow[\text{[I]}]{\underset{\text{CH}_3\text{C-COOCH}_3}{\overset{\text{CH}_2}{\parallel}}}
$$

The starting reagent in this method, ar-chloromethyl-styrene [A] was prepared using the procedure described by Clarke (ref. 13).

$$
\text{C}_6\text{H}_5\text{-}C_2H_5 + CH_2O + HCl \rightarrow \text{[para-}C_2H_5\text{, }CH_2Cl\text{]} + \text{[B] (ortho-}C_2H_5\text{, }CH_2Cl\text{)}
$$

$$
\text{[B]} + Br_2 \xrightarrow{\text{UV}} \text{[D] (}BrCHCH_3\text{, }CH_2Cl\text{)} \xrightarrow{\Delta} \text{[A] (}CH=CH_2\text{, }CH_2Cl\text{)}
$$

The product [A] consists of about 70% *para* isomer and 30% *ortho* isomer.

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The reaction schemes, I and II, were tested using the ligand, α-aminomethylpyridine. For example, poly(vinylbenzyl-2-pyridylmethylamine)-methyl methacrylate copolymer, where LH is

CH₂-NH₂, was prepared by both routes. A higher molecular weight polymer (softening range 120-140°C, and relative viscosity of 1% solution, 1.15) was obtained by Route I. The rate of polymerization of vinylbenzyl-2-pyridylmethylamine with methyl methacrylate (Route II) was extremely low and the low molecular weight product isolated after 80 hours at 80°C had a softening range 75-100°C (relative viscosity of 1% solution, 1.05). The rate of homopolymerization of this monomer at 80°C was also low.

Several 8-hydroxyquinolines with >NH substituents were also prepared and reacted with chloromethylated polystyrene. Amides and sterically hindred amines such as the following compounds did not react: 5-t-butylaminomethyl-8-hydroxyquinoline, 7-[α-(5-methyl-2-pyridylamino)benzyl]-8-hydroxyquinoline, 5-(N-benzamido-methyl)-8-hydroxyquinoline. The methods we used to prepare these compounds are described in the Experimental section.

A sterically open amine, 5-aminomethyl-8-hydroxyquinoline, was prepared by the following route.
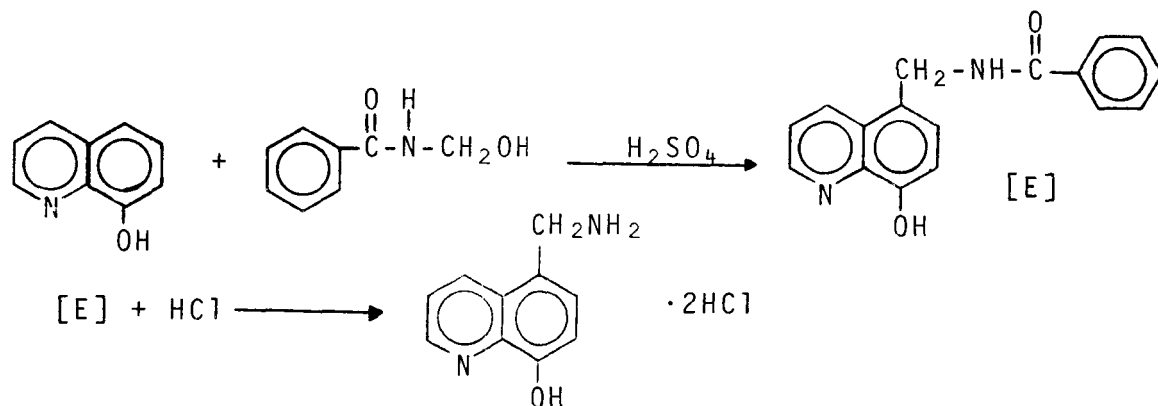
We found that yields of product by this route through the benzyl-amide were greater than via the corresponding acetylated compound.

The free amine was obtained by neutralizing the hydro-chloride with ammonium hydroxide immediately before use. This amine reacted readily with chloromethylated polystyrene in ethyl acetate solution. There was some disubstitution that crosslinked the product.

6. Pyridine-Containing Ligands with Small Ring Chelation Sites

A pyridine-acid ligand group with a 7-membered ring can be incorporated into a polymer via 2-pyridylacrylic acid. This monomer does not homopolymerize, but is known to copolymerize with acrylonitrile (ref. 14). A sample of 2-pyridylacrylic acid was prepared by reaction of 2-pyridine aldehyde with malonic acid using a procedure described by Marvel et al (ref. 14). However, in two attempts to prepare the copolymer by emulsion polymerization with persulfate and with azo-bis-isobutyronitrile catalyst, no usable polymer was obtained.

We also attempted to prepare the ligand-monomer, 2-vinyl-6-aminopyridine, by following the reaction sequence described by Cislak (ref. 15).
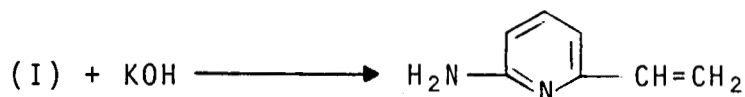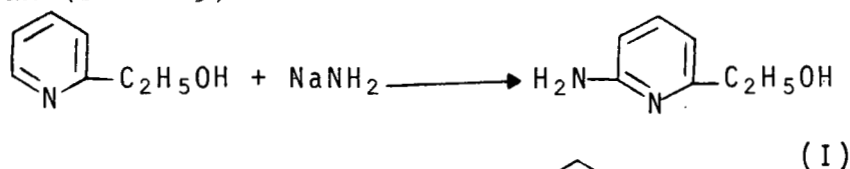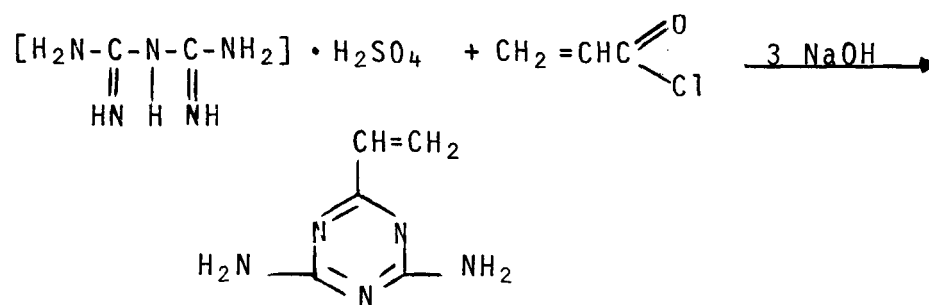

Attempts to prepare the intermediate, 2-amino-6-ethanol-pyridine (I), yielded only polymeric products together with distillable products that contained neither amino nor hydroxyl substituents. The preparation of this intermediate was tried using both dimethylaniline and xylene as solvents.

7. Iminodiacetic Acid Ligand on Polystyrene

The homopolymer, poly[N-(ar-vinylbenzyl)iminodiacetic acid] was prepared to determine the stability of the iminodiacetic acid group in 40% KOH. The polymer was prepared from its monomer by polymerization with persulfate catalyst in water. The monomer was prepared by reaction of the sodium salt of iminodiacetic acid with chloromethylvinylbenzene using a procedure described by Morris (ref. 16).

8. Polymers from 4,6-Diamino-2-Vinyl-s-Triazine

4,6-Diamino-2-vinyl-*sym*-triazine was prepared by reaction of biguanide sulfate with acrylyl chloride in basic meduim (ref. 17).

$$[H_2N-\underset{\underset{HN}{\|}}{C}-\underset{\underset{H}{|}}{N}-\underset{\underset{NH}{\|}}{C}-NH_2] \cdot H_2SO_4 \quad + \quad CH_2=CHC\underset{Cl}{\overset{O}{\diagup}} \quad \xrightarrow{\ 3\ NaOH\ }$$

The monomer polymerized readily in aqueous solution with persulfate catalysis. An attempt to copolymerize this monomer with methyl methacrylate was unsuccessful.

IV. EXPERIMENTAL

A. SYNTHETIC METHODS

1. Preparation of CO- and Terpolymers Containing 2-Vinylpyridine

These polymers were prepared by bulk polymerization with freshly distilled monomers at 60°C with 0.05% azo-bis-isobutyronitrile catalyst in a nitrogen atmosphere. Reactants were stirred during the heating period, the length of which was chosen to give approximately 30% conversion. The polymers were purified by three successive precipitations with a non-solvent from solution and dried in vacuum. Properties of individual polymers are listed in Table 9.

2. Preparation of Styrene:Maleic Anhydride:Methyl Methacrylate Terpolymers

a. Preparation

These polymers were prepared by bulk polymerization at 60°C with 0.02% azo-bis-isobutyronitrile catalyst in nitrogen atmosphere. Maleic anhydride was purified by recrystallization from chloroform; the other two monomers were freshly distilled. Reactants were stirred during the heating period, the length of which was chosen to give approximately 30% conversion. The polymers were purified by three successive precipitations with a nonsolvent from solution and dried in vacuum. Properties of individual polymers are listed in Table 9.

b. Analysis

Neutralization equivalents of the terpolymers were determined as follows: (1) dissolve weighed sample of about 0.35 g in acid-free acetone; (2) add 35 ml of standardized 0.1 N NaOH; (3) shake mixture two hours at room temperature; and (4) back-titrate to phenolphthalein end-point with standardized 0.1 N HCl. Neutralization equivalents found were:

>   10024A: 144
>   10024B: 163, 159
>   10044 : 125, 129

3. Preparation of Substituted Ligands Used in Coupling Reactions

a. Preparation of 5-Chloromethyl-8-hydroxyquinoline Hydrochloride

The procedure described by Burckhalter and Leib (ref. 18) was used to prepare this compound. Hydrogen chloride gas was bubbled into a stirred mixture of 435 g (3 moles) of 8-hydroxy-

quinoline, 480 ml of conc. HCl and 480 ml of 3% aqueous formaldehyde for 4 hours. The mixture was cooled, and the yellow solid product was collected on a filter and dried. The product melted with decomposition at 278°C.

b. Preparation of 5-tert-Butylaminomethyl-8-hydroxyquinoline

5-Chloromethyl-8-hydroxyquinoline (46 g, 0.2 mole) was added at room temperature to a solution of 73.1 g (1.0 mole) of t-butylamine in 1500 ml of ethyl acetate. When the slight exotherm subsided, the mixture was heated with stirring on a steam bath at about 60°C for 1 hour. The precipitated t-butylamine hydrochloride was filtered and washed twice with ethyl acetate. The ethyl acetate filtrates were flash evaporated leaving a greenish solid-oil, which was extracted with 200 ml of diethyl ether. The ether was flashed off leaving an oil that solidified overnight. The solid was recrystallized from hexane and then vacuum dried. The product (19.2 g) was an off-white solid melting at 65-70°C. IR and NMR spectra were consistent for the above structure.

c. Preparation of 5-(N-Methyl-N-acetaldehydediethylacetal aminomethyl)-8-hydroxyquinoline

Methylaminoacetaldehyde diethyl acetal (44.1 g, 0.3 mole) was added to a stirred slurry of 22.6 g (0.1 mole) of 5-chloromethyl-8-hydroxyquinoline hydrochloride in 200 ml of ethyl acetate at room temperature. The mixture was heated and refluxed for 2.5 hr and then was cooled. The hydrochloride by-product that separated was collected on a filter and the filtrate was evaporated. The residue was triturated with hexane. Its NMR spectrum was in agreement for the above named compound.

d. Preparation of 7[α-(5-Methyl-2-pyridylamino)benzyl]-8-hydroxyquinoline

The procedure described by J. Phillips et al (ref. 19) for preparation of this Mannich base was followed on a twenty-four fold scale.

Benzaldehyde (51.0 g, 0.48 mole) and 2-amino-4-methylpyridine (51.8 g, 0.48 mole) were dissolved in 1100 ml of 95% ethanol. Then, after complete dissolution, 8-hydroxyquinoline (69.6 g, 0.48 mole) was added, forming a clear yellow-orange solution. The product that had precipitated after four days was collected and recrystallized from a 1:1 mixture of ethanol and acetone. The yield was 16.0 g of a white solid (mp 188-189°C). Phillips et al. report mp 158°C. However, the NMR spectrum of our product was consistent with the desired structure and we believe the 158°C value is a typographical error.

e. Preparation of 5(4-Hydroxybutoxymethyl)-8-hydroxyquinoline

A mixture of 46 g of 5-chloromethyl-8-hydroxyquinoline hydro-
chloride, 100 ml of 1,4-butanediol, and 16 g of sodium bicarbonate
were mixed, shaken, and left at room temperature for 2.5 hr. The
slurry was heated overnight at 90°C and then poured into water.
The mixture was made basic with ammonia, and insoluble by-products
were removed by filtration. The filtrate was neutralized with
acetic acid and the precipitated product was collected on a
filter, washed with water, and dried in vacuum. Its NMR spectrum
was consistent for the above named product.

f. Preparation of 5-Benzamidomethyl-8-hydroxyquinoline

(1) Preparation of Methylolbenzamide

The method described by E. Beschkopff (ref. 20 was followed
on a two fold scale.

Formaldehyde (37%, 90 g) was added slowly with stirring to a
mixture of benzamide (140 g), potassium carbonate (4 g), and water
(140 g). This was warmed on a steam bath until a solution resulted,
then allowed to cool. Collection of its precipitate and recrystal-
lization from ethanol yielded 80.4 g of a white crystalline solid.
Its NMR spectrum indicates the desired product.

(2) Coupling Reaction

The method of preparation described by Einhorn was followed
(ref. 20 and 21).

8-Hydroxyquinoline (0.2 m, 29.0 g) was added over 45 minutes
to concentrated sulfuric acid (250 ml) at -5°C with stirring.
Then methylolbenzamide (0.2 m, 30.2 g) was added over 45 minutes
at -5°C. This was allowed to come to room temperature slowly and
stirring continued for two days. The clear yellow solution was
poured slowly into an ice-water mixture. The resulting yellow,
sticky semi-solid was extracted with 100 ml of 5% sodium hydroxide
solution. This was treated with pieces of Dry Ice and the pre-
cipitate that formed was filtered off and recrystallized from
ethanol. This yielded, after vacuum drying, 3.0 g (mp 174-176°C).
An NMR spectrum indicates the deisred compound.

g. Preparation of 5-Aminomethyl-8-hydroxyquinoline Dihydro-
chloride

The preparation method described by Monti and Verona was
used (ref. 22).

5-Benzamidomethyl-8-hydroxyquinoline (17.0 g) was refluxed
in concentrated hydrochloric acid (125 ml) for five hours. The
solution was chilled and the solid product collected on a filter.

It was washed with 500 ml of cold ethanol and then with 300 ml of diethyl ether and dried under vacuum. The yellow solid product weighed 8.1 g and melted at 250°C (d). Its NMR is consistent with the desired product.

h. Preparation of 8-Hydroxy-5-acetaminomethylquinoline

(1) Preparation of Methylene Bis-N-Acetamide

The method described by R. C. Brian and A. H. Lamberton (ref. 23) for reaction of acetamide with formaldehyde was followed on the same scale. The crystallized white solid weighed 63 g (mp 205-208°C). An NMR spectrum was consistent with the desired product.

(2) Coupling Reaction

Methylene-bis-acetamide and 8-hydroxyquinoline were reacted with phosphorus oxychloride using a procedure by M. Ishidate et al (ref. 24) scaled up seven fold. The reaction was heated on a steam bath for 2 hours. The recrystallized solid yielded about 1 g of product (mp 187-188°C). An NMR spectrum indicated the desired product.

Two other preparations were carried out using longer reaction times and with chloroform as solvent. Yields were not increased by these variations of reaction conditions.

4. Chloromethylation of Polystyrene

a. High Molecular Weight Polystyrene

A solution of 4.5 ml of anhydrous stannic chloride in 135 ml of chloromethylmethyl ether was added dropwise over 1 hour to a stirred solution of 36 g of polystyrene (Lustrex®) in 3600 ml of dichloroethane at 50°C under nitrogen. The solution was stirred for 8 hours at 50°C and 13 hours at room temperature and then poured into a total of 7 liters of methanol. The white precipitate was filtered off, slurried in 1500 ml of methanol for 30 min with fast stirring and then filtered. This methanol wash was repeated three times and the resulting solid was vacuum dried overnight at 52°C. This yielded 45.3 g of a pale yellow solid. Analysis Found: C, 80.0; H, 6.9; Cl 12.2. This corresponds to 42.2% substitution by the chloromethyl group. A similar reaction on a smaller scale gave product with 36% substitution.

b. Polystyrene With Molecular Weight 20,000

A low molecular weight polystyrene (mw 20,000) was chloromethylated using the same procedure. This yielded 44.7 g of a pale yellow solid. Analysis found: C, 79.0; H, 5.7; Cl, 13.0; ash, 0.0. This corresponds to 46.6 mole-% substitution by the chloromethyl group.

5. Coupling Reactions of Chloromethylated Polystyrene With Ligands

a. Preparation of Polyvinylbenzyl-2-(2-pyridylethyl)amine

Chloromethylated polystyrene from Lustrex® (3.8 g) dissolved in 150 ml of p-dioxane was added dropwise at room temperature to a stirred solution of 15.3 g of 2-(2-aminoethyl) pyridine in 150 ml of p-dioxane. The solution was refluxed for 18 hours. On cooling, a precipitate formed, which was filtered off, dried, and identified as the hydrochloride from its IR spectra. Hexane (300 ml) was added to the stirred filtrate and the resulting precipitate was collected by centrifugation. The solid was dissolved in p-dioxane and reprecipitated with hexane, and collected by centrifugation. It was then dried under vacuum for 23 hr at 40°C and 17 hr at 56°C. The extended drying period was necessary to remove the last traces of dioxane. Product weighed 2.7 g and had a negative Beilstein test for chlorine. Analysis found: C, 84.4; H, 7.8; N, 6.2.

b. Preparation of Polyvinylbenzyl-2-pyridylmethylamine

2-Aminomethylpyridine (13.5 g, 0.125 mole) dissolved in 100 ml of p-dioxane was added dropwise at room temperature to chloromethylated polystyrene (3.0 g) that contained 42% chloromethyl substituent dissolved in 150 ml p-dioxane. This was heated to reflux for 17 hours. The hydrochloride that precipitated was collected on a filter and the filtrate was poured slowly into 800 ml of fast stirring hexane. The product that precipitated was centrifuged, washed with hexane twice and methanol once, and dried in a vacuum desiccator. Yield was 4.3 g of an orange solid which gave a negative Beilstein test for chlorine. Analysis found: C, 84.8, H, 7.5; N, 6.1.

c. Preparation of Polyvinylbenzyl-1-(β-aminoethyl)-2-methyl-2-imidazoline

Chloromethylated polystyrene (3.8 g) dissolved in 150 ml of p-dioxane was added dropwise at room temperature to a stirred solution of 1-(β-aminoethyl)-2-methyl-2-imidazoline (15.9 g, 0.125 mole) in 100 ml p-dioxane. The solution was refluxed for 5 hours and then cooled.

A precipitate that formed was collected on a filter, triturated with methanol twice, and vacuum dried overnight at 60°C yielding 4.8 g of a yellow solid. Analysis found: C, 77.1; H, 8.2; N, 8.2.

d. Preparation of Polyvinylbenzylcatechol

A solution containing 6 g of chloromethylated polystyrene (Lustrex® - 42% substitution), 6 g of catechol, and about 0.2 g of fused zinc chloride in 130 ml of dioxane was stirred at reflux

for six hours. The solution was cooled and poured into methanol. The precipitate was collected, washed with water, and dried in a vacuum.

e. Preparation of Polyvinylbenzylsalicylic Acid

Salicylic acid (5 g), chloromethylated polystyrene with 42% chloromethyl substitution (5.3 g) and freshly fused zinc chloride (5.5 g) in 75 ml dioxane were heated to reflux and refluxed for 18 hours. The reaction solution was cooled and poured with stirring into methanol. The mixture was centrifuged and the solid triturated with dioxane. The dioxane solution was poured into methanol, the precipitated product removed by centrifuging, and dried at room temperature in vacuo. Yield was 3.2 g. Analysis found: C, 79.5; H, 6.8; Cl, 1.2.

f. Reaction of Chloromethylpolystyrene With 5-(4-Hydroxy-butoxymethyl)-8-hydroxyquinoline, 5-t-Butylaminomethyl-8-hydroxyquinoline), and 5-Aminosalicylic Acid (Attempted)

Reaction conditions were identical to those used with 2-(2-aminoethyl) pyridine for each of the above reactants. Only unreacted starting materials were recovered. The chloromethyl group was readily identified by its strong absorption at 8.0 μ.

A second similar reaction with 5-(4-hydroxybutoxymethyl)-8-hydroxyquinoline was run in pyridine solution. Product isolated was insoluble in pyridine, indicating that by-product crosslinking occurred. However, it still contained a large degree of chloromethyl substitution.

g. Attempt to React Chloromethylated Polystyrene with 5-(Benzamidomethyl)-8-hydroxyquinoline

Chloromethylated polystyrene (ca 100,000 molecular weight) (3.1 g, 0.02 mole) was dissolved in 50 ml of pyridine and added dropwise at room temperature to 5-(benzamidomethyl)-8-hydroxy-quinoline (5.3 g, 0.02 mole) in 50 ml of pyridine. The solution was heated at 60°C for an hour when a precipitate formed. This was filtered off and the pyridine solution flashed yielding 3.8 g of the starting material 5-(benzamidomethyl)-8-hydroxyquinoline. The filtered precipitate was soluble in water.

h. Attempts to React Chloromethylated Polystyrene and 7-[α-(5-Methyl-2-pyridylamino)benzyl]-8-hydroxyquinoline

Chloromethylated polystyrene (ca 100,000 molecular weight) (6.1 g, 0.04 mole) was dissolved in 75 ml of benzene and added over 40 minutes at 50°C to a solution of 7-[α-(5-methyl-2-pyridylamino)benzyl]-8-hydroxyquinoline (13.6 g, 0.04 mole) in 550 ml of benzene and 16 ml of pyridine. This was reacted for 24 hrs at 60°C. On cooling, a precipitate formed which yielded

approximately 12 g of the starting 7-[α-(5-methyl-2-pyridylamino)benzyl]-8-hydroxyquinoline.

A similar reaction was carried out in refluxing dioxane with the same result.

i. Preparation of 4-(5-Methylene-8-hydroxyquinolino)-vinylbenzene-Styrene Copolymer

5-Chloromethyl-8-hydroxyquinoline hydrochloride (15.5 g, 0.05 mole) was added with stirring to a cooled solution of 10.42 (0.1 mole) polystyrene (molecular weight 20,000) in 200 ml of nitro-benzene contained in a flask protected by a drying tube. The slurry was stirred at 5 to 10°C while 8 g (0.06 mole) AlCl$_3$ was added in portions. The resulting solution was stirred 2 hours at 10°C and 19 hours at 65°C, and then poured onto ice. The resulting precipitate was collected and boiled in two successive batches of 10% HCl for 3-hour periods. A small amount of occluded nitrobenzene was removed by steam distillation during the first period. The precipitate was then collected and slurried in dilute aqueous NaOH that was then neutralized with acetic acid. The solid was collected again and recrystallized twice from pyridine and once from benzene. A benzene-insoluble by-product was separated from product at this stage. Final product was dried at 60°C/0.4 mm. Its softening range was 123 to 143°C. Nitrogen analysis: found, 1.5%.

6. Preparation of Polystyrene-Diazonium Chloride

a. Polynitrostyrene [Method No. 1]

Linear polystyrene (50 g, <50 mesh) was added over 40 minutes to a stirred solution of 140 ml of nitric acid (sp gr 1.42) and 350 ml of sulfuric acid (sp gr 1.84). The temperature was kept at 65-75°C for an additional 90 minutes. The mixture was poured into 2 liters of ice water, filtered, and washed until neutral. The yellow product was allowed to air dry, yielding 85 g of nitrated product.

Analysis of products prepared from this intermediate shows that it is a mixture of mono- and dinitro-substituted polymers. Method 2 described in Section V, 9.a gives monosubstituted products.

b. Polyaminostyrene

The nitrated product from above was added with stirring to stannous chloride (400 g), concentrated hydrochloric acid (450 ml) and methanol (500 ml) and refluxed at 78°C for 22 hours.

The brown-black swollen solid was collected on a filter and washed with water. The solid was then stirred in one liter of 2N sodium hydroxide for an hour, filtered, and washed with water until the wash was neutral.

c. Polystyrene-Diazonium Chloride

The polyaminostyrene was stirred in a liter of 2N hydrochloric acid for 30 minutes to convert it to the hydrochloride. The swollen solid was separated and washed with water to remove excess acid and aqueous colorations.

The swollen amine hydrochloride was divided into two parts for convenience. Each part was stirred in 2 liters of water and cooled to 0-5°C, forming a brownish gel. Over a period of 6 hours, 1M sodium nitrite (grand total 400 ml) and 1M hydrochloric acid (grand total 400 ml) were added in portions in equal amounts. The reaction progress was followed with starch-iodide paper. The swollen solid was allowed to settle and the aqueous decanted. The solids from the two diazotisations were combined and washed with water while keeping the temperature near 5°C.

The wet, reddish-brown solid was divided into three equal parts and placed in a freezer until used in the preparations described below.

7. Preparation of Polystyrene-azo-salicylic Acid

The polystyrene-diazonium chloride previously prepared was added over 40 minutes to a stirred solution of salicylic acid (17.3 g, 0.125 mole) in 500 ml of 10% sodium hydroxide chilled to 3-4°C. This was reacted for 16 hours at 0-5°C. Then the reaction mixture was filtered and washed thoroughly with cold water until almost neutral. The solid was dried under vacuum yielding 15 g of a very fine, brownish solid.

8. Preparation of Polystyrene-azo-8-hydroxyquinoline

This preparation was the same as that for polystyrene-azo-salicylic acid except that 8-hydroxyquinoline (18.2 g, 0.125 mole) was used. This yielded 14 g of a dark brown solid.

9. Preparation of Poly-[N-(2-pyrimidyl)aminostyrene]

a. Poly(p-nitrostyrene) [Method 2]

A method by H. Zenftman (ref. 12) was followed. A mixed acid (500 g) composed of HNO_3 (72%), H_2SO_4 (19%), H_2O (9%), was cooled to -3°C and 30 g of linear polystyrene was added. The temperature was increased to 20°C and held there for 75 minutes. During this time the polystyrene dissolved, forming a light orange solution. The solution was then slowly poured into 3 liters of rapidly stirred ice water. The resulting orange solid was collected on a filter and washed with large volumes of water until the washings were neutral.

b. Poly(p-aminostyrene)

The poly(nitrostyrene) from above was reacted with 500 ml of methanol, 250 g of stannous chloride, and 270 ml of concentrated hydrochloric acid at reflux for 17 hours. The reaction mixture was poured into 3.5 liters of rapidly stirred ice water and made basic with 10% sodium hydroxide. This precipitated a large amount of a flocculent solid. After 2 hours, the aqueous portion was decanted and the solid was washed until neutral. The wet solid was vacuum dried yielding 32 g. Its spectrum in the infrared showed no nitro absorption at 7.5 μ. Analysis indicated a small amount of tin oxide was still occluded in the polymer.

Analysis: Found: C, 71.1; H, 7.3; N, 11.8; Ash, 5.4.
Cal'c. for C_8H_9N: C, 80.5; H, 6.1; N, 11.8.

c. Coupling of Poly(aminostyrene) With 2-Chloropyrimidine

2-Chloropyrimidine (5.7 g, 0.05 mole) was dissolved in 50 ml of pyridine and was added dropwise at room temperature to poly-(aminostyrene) (6.0 g, 0.05 mole) in 200 ml pyridine. The reaction mixture was then heated at reflux for 17 hours. The dark red solid that separated was collected on a filter and washed successively with 250 ml of methanol, 500 ml of 0.1 N sodium hydroxide, and water. It was then vacuum dried overnight at 60°C yielding 8.6 g of a fine red powder. A Beilstein test for chlorine was negative.

10. Polymers and Copolymers Derived From ar-Chloromethylvinyl-benzene

a. Preparation of ar-Chloromethylvinylbenzene

The preparation method reported by Clarke and Hamerschlag (ref. 13) was followed. Chloromethylation of 800 ml of ethyl-benzene with 60 g of paraformaldehyde, 40 g of anhydrous zinc chloride catalyst, and a continuous stream of anhydrous HCl for a period of 75 min. at 60-70°C yielded 80 g of isomeric product. NMR and VPC analysis indicated this product consisted of 96% chloromethylethylbenzene with ortho para ratio 0.30:0.70.

The entire amount of chloromethylethylbenzene was brominated and then dehydrobrominated by distillation. The yield of redis-tilled ar-chloromethylvinylbenzene was 32 g.

b. Vinylbenzyl-2-pyridylmethylamine and Its Polymers

(1) Preparation of Vinylbenzyl-2-pyridylmethylamine

A solution of 15.2 g (0.1 mole) of ar-chloromethylvinylbenzene inhibited with hydroquinone in p-dioxane (25 ml) was added dropwise over 30 minutes to 2-aminomethylpyridine (32.4 g, 0.3 mole) in p-dioxane (100 ml), and the resulting solution was heated at

reflux for 16 hours. The reaction pot was chilled and the pre-
cipitated hydrochloride filtered off. Solvent and excess amine
were distilled at 11 mm. The residue was a thick orange syrup
(20.3 g), which had an IR spectrum characteristic of the desired
compound.

This residue was dissolved in 80 ml of benzene. The benzene
solution was washed with aqueous 10% sodium hydroxide to remove
inhibitor, then was washed with several portions of water, and
finally was dried over calcium chloride. The benzene solution
was then divided in half and used in the following polymerizations.

(2) Homopolymerization of Vinylbenzyl-2-pyridylmethyl-amine

The above benzene solution was heated at 60-80°C with a total
of 100 mg of azo-bis-isobutyronitrile for 80 hours. The benzene
was distilled off at 60 hours to aid polymerization.

The resulting syrup was dissolved in 25 ml of benzene and
poured into stirring hexane. The resulting precipitate was re-
precipitated twice more with the benzene/hexane solvent/non-solvent
pair and then dried in a vacuum at 60°C. The product yield was
1.2 g.

(3) Copolymerization of Vinylbenzyl-2-pyridylmethylamine With Methyl Methacrylate

The benzene solution of vinylbenzyl-2-pyridylmethylamine
prepared above and 5 g of distilled methyl methacrylate was poly-
merized with 100 mg of azo-bis-isobutyronitrile catalyst for 60
hours at 60-80°C. Benzene/hexane was the solvent/non-solvent
pair used for precipitation. The product weighed 1 g after drying
at 60°C in vacuum. It softened at 95°C.

(4) Preparation of Poly(Vinylbenzyl-2-pyridylmethyl-amine)-Methyl Methacrylate Copolymer

2-Aminomethylpyridine (9.2 g) dissolved in 50 ml of p-dioxane
was added dropwise over 25 minutes at room temperature to vinyl-
benzyl chloride-methyl methacrylate copolymer (4.0 g) in 150 ml
of p-dioxane. This was heated at reflux for 18 hours. On cooling,
the hydrochloride precipitate was filtered off and the filtrate
was poured slowly into a liter of stirring hexane. The brownish
precipitate that formed was dissolved in benzene and again pre-
cipitated in hexane. This was insoluble in benzene but was soluble
in methanol. It was triturated with diethyl ether, yielding 3.2 g
of a light orange solid. A Beilstein copper wire test for chlorine
was negative.

Analysis: C, 71.1; H, 7.4; N, 8.3 corresponds to 60.9 mole-%.
MMA: 39.1 mole-% vinylbenzyl-2-pyridylmethylamine.

11. Poly-(4,6-Diamino-2-Vinyl-s-triazine)

a. Preparation of 4,6-Diamino-2-vinyl-s-triazine

The method of preparation of this compound described by Overberger and Michelotti (ref. 17) was followed with 0.6 mole of biguanide sulfate. The yield of product after recrystallization from water was 11.8 g.

b. Homopolymerization of 4,6-Diamino-2-vinyl-s-triazine

Monomer (3.4 g) was polymerized with 10 mg of potassium persulfate initiator following the procedure described by Overberger and Michelotti (ref. 17). The polymer was washed with ethanol and dried at 50°C/1 mm overnight. The yield was 3.0 g.

12. Poly[N-(ar-vinylbenzyl)iminodiacetic Acid]

a. Preparation of N-(ar-Vinylbenzyl)iminodiacetic Acid

The preparation method described by L. R. Morris (ref. 16) was followed on a 0.1-mole scale. Recrystallized product weighed 5 g. Its NMR spectrum is in excellent agreement for the above-named compound.

b. Homopolymerization of N-(ar-Vinylbenzyl)iminodiacetic Acid

Potassium persulfate (14 mg) was added to a clear, slightly yellow solution of N-(ar-vinylbenzyl)iminodiacetic acid (4.5 g) dissolved in 500 ml of water, and then heated to reflux (100°C) for 5 days. During the second day an additional 30 mg of potassium persulfate was added. Isolation of the polymer yielded 2.5 g of a slightly yellow powder.

13. Preparation of β-(2-Pyridyl)acrylic Acid

The method reported by C. S. Marvel et al (ref. 14) was followed. Malonic acid (31.4 g, 0.3 mole), freshly distilled 2-pyridine aldehyde (32 g, 0.3 mole), pyridine (23.7 g, 0.3 mole) and piperidine (6 drops) were added to a round-bottomed flask fitted with a condenser and reacted on a steam bath for 2 hr 15 min. On cooling, a solid separated that was collected on a filter, washed twice with cold water, and finally dried under vacuum at 70°C, yielding 4.8 g of an off-white powder (mp 203°C dec; lit (ref. 14) mp 198°C dec).

14. Preparation of N-Octyl Half Ester of Styrene-Maleic Anhydride Copolymer

Lytron® 810 resin (20.2 g) and 13 g n-octyl alcohol were heated at 100-105°C for 18 hours under a condenser. The polymer

was precipitated three times from acetone/hexane solvent/non-solvent combination. The acid number of the product was 453.

B. TEST METHODS

1. Thermal Gravimetric Analysis

Isothermal gravimetric changes were measured in nitrogen during 60 hours exposure of polymer samples at 135°C. Weighed samples of approximately 0.2 g were placed in tared porcelain microcrucibles, which were suspended by Nichrone wire from a Roller-Smith Precision balance into a heated tube through which a continuous stream of nitrogen flowed at 200 ml/min. Temperature was controlled by a Sim-Ply-Trol Pyrometer to 135 ± 2°C. The thermocouple sensor was placed within one inch of the sample.

2. Electrical Resistance of Membranes

The general procedure described by Salkind and Kelley (ref. 25) for measuring electrical resistance in 40% KOH was followed. Measurements were made with a Wayne-Kerr Component Bridge, Model B522. The resistance cell is essentially as described in reference 25 but includes the latest improvements made by the ESB personnel. Measurements were made on membranes after soaking overnight in 40% KOH.

3. Zinc Penetration Test

A test procedure similar to that described by Dalin and Solomon (ref. 26) was used. The test cell is identical to theirs. Current (10 ma) was supplied by an Acopian Model K-55 Power Supply with a rheostat and metered by a Weston Model 911 d-c milliammeter. Traversal is the time required for the voltage to drop below 1 volt. This time was measured by conveying the reference voltage from a Hewlett-Packard Model 412A d-c vacuum tube voltmeter to a Simpson meter relay that activates an Eagle signal timer at this shut-off voltage.

The separators were presoaked for at least 16 hours in the test solution, 1M ZnO in 40% KOH.

4. Pore Size Determination by Electrolyte Permeability

The method developed by Salkind and Kelly (ref. 27) was used. The 2-mm capillary tube of the apparatus is joined to a 18/9 O-ring joint with 0.785 cm cross-sectional area. The separators were held between two Neoprene O-rings clamped in the joint. Constants of 40% KOH electrolyte used to calculate pore radius, r, were 1.396 g/cc density and 0.033 g/cm-sec viscosity. All samples were presoaked overnight in electrolyte before testing.

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Data obtained by measuring adsorbance of electrolyte, pore size, electrical resistance, and dimensional changes after soaking in electrolyte were used to calculate effective porosity and to estimate the tortuosity of the pores. The tortuosity factor was calculated by the equation (ref. 28):

$$TF = \sqrt{\frac{\rho_{membrane}}{\rho_{KOH}} \text{(Effective Porosity)}}$$

5. Tensile Strength of Membranes

Tensile specimens were prepared by stamping out 1 x 5 in. samples of our polymer films with a steel rule die. These specimens were tested in an Instron-Tensile Tester equipped with one inch "T" grips having sandpaper liner. The grip separation was 2.75 ± 0.25 in. and the crosshead speed was 0.5 in./min unless noted otherwise. Wet thickness was used to calculate strengths of wet membranes. Data are summarized in Table 3.

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